DEVELOPMENT OF ZIRCONIUM- AND STAINLESS STEEL-BASED COMPOSITES FOR MANUFACTURE OF ADAPTERS TO NPP STRUCTURES

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The paper describes the developed composite materials produced with application of solid-phase welding. Zr1Nb–08Kh18N10T composites with different interlayers were manufactured in the vacuum rolling mill. Their physico-mechanical properties were studied after rolling, heat treatment, corrosion testing and electron bombardment. Zr1Nb–08Kh18N10T composite with nickel interlayer was selected as the most promising for further investigations.

Keywords: *vacuum rolling, layered composites, zirconium, stainless steel, adapters, microstructure, strength, heat treatment, corrosion, barrier interlayers, adapter elements*

The joints from dissimilar metals and alloys, which are different in composition and physico-mechanical properties, are used in assembly units of the structures in many branches of industry, including nuclear-power engineering. Mechanical, thread-brazing methods or fusion welding are used for making such joints.

The fuel elements (FE) of series of reactors have permanent joints from zirconium to 08Kh18N10T stainless steel. Obtaining of high strength and safe joints from these metals using fusion welding is not possible since they are metallurgically incompatible. Brittle intermetallic phases appear at that on the boundaries of components of composites and can grow up to critical sizes under the action of significant heat flows that leads to a formation of macro and microcracks in the joint zone and then to complete loss of a structure integrity.

We developed and manufactured the adapters from zirconium alloy Zr1Nb and stainless steel 08Kh18N10T [1–3] using solid-phase welding with the aim to increase a life time and safe operation of aggregates and separate assembly units of the structure of NPP reactors. Safety and life time of composite products can be provided through an introduction of barrier and damping interlayers on the boundaries of the main components in composition of layered composites.

The present paper studied physico-mechanical properties of composite materials Zr1Nb with 08Kh18N10T through single interlayers of nickel or niobium as well as double interlayers of niobium or vanadium from the side of zirconium and copper or nickel from the side of stainless steel (SS) depending on time and temperature of annealing, corrosive environment as well as under conditions of electron bombardment.

Solid-phase welding of 08Kh18N10T type SS with Zr1Nb alloy was performed on Duo-170 vacuum rolling mill of a design of the NSC «Kharkov Institute of Physics and Technology» after modernization of a range of assembly units [4].

Metallographic investigations were carried out on optical microscope GX-51 of «Olympus» company with IA-32 picture analyzer. Microhardness of composite components were measured on the LECO LM-700AT digital micro hardness gage.

Mechanical properties of the composites were studied on cylinder samples cut out from composites along the whole thickness perpendicular to the boundaries of layers joining. Diameter of test portion of the samples made 4 mm and its length was 20 mm. The tests were performed on a tensile-testing machine at temperature of 20 °C with transverse speed of a moving holder of 2 mm/min. Test procedure corresponded to GOST 1497–84. The flat samples of 35 × 8 × 1 mm size were used during tests of bombarded samples to layers separation.

Corrosion tests were carried out by means of autoclaving method at a temperature and pressure, simulating working parameters, in liquid medium corresponding in composition to real conditions in the reactor [5]. Water, cleaned by means of double distillation, close in composition to working fluid of a primary coolant circuit of a can of reactor FEs of NPP was used in autoclave testing. The temperature made 350 °C and water pressure was 16.5 MPa. The microsections for investigation of corrosion process in time were polished and studied in a course of 50, 100, 500 and 1000 h after the tests without preliminary etching of composites' structure with the aim to trace surface changes of their components after corrosion. The bombardment of composites was carried out with 10 MeV energy electrons of $(3.3–330)\cdot 10^{20}$ el/m^2 dose on an accelerator KUT-1 of a design of the NSC «Kharkov Institute of Physics and Technology».

Analysis of the data of study [6] about a nature of materials joining in solid phase as well as the factors having influence on adhesive strength of layers in composite materials gives the basis to state that the mechanical properties of permanent joints are determined by initial properties of composite components as well as significantly depend on technological parameters, i.e. residual gas pressure in a chamber at heating and rolling, temperature, reduction of cross-sectional area of package, deformation rate. Besides, a level of structural and mechanical inhomogeniety and peculiarities of stress-strain state of the material near the boundaries of joining of composite components have an influence on adhesion strength.

We did not succeed in a selection of any barrier intermediate interlayer, except double Nb–Cu, which forms a series of continuous solid solutions with zirconium and SS, in studying constitutional diagrams of binary alloys [7, 8]. All other metals used as an interlayer between zirconium and SS form intermetallic compounds at different temperature of heating. This factor limits a selection of maximum temperature of hot vacuum rolling by values of temperature at which formation of brittle intermetallic phases on the boundaries of joining of composite components took place. It follows from the analysis given above that the double interlayers Nb–Cu and V–Ni and single interlayers of niobium and nickel were selected as the most perspective.

Width of the package made 65–70 mm and its length was 150–200 mm, thickness of zirconium and steel 08Kh18N10T made 15–20 mm (for each package), thickness of intermediate interlayers in the initial condition was 1.5–2.0 mm.

The following parameters of the rolling process were selected as the most optimum conditions for obtaining Zr1Nb–08Kh18N10T composites based on experimental data: residual pressure in furnace chamber of $(1-5)\cdot10^{-3}$ Pa; reduction of cross-sectional area of (30 ± 2) %; furnace temperature of (900 ± 50) °C.

The microstructure of composite materials immediately after hot vacuum rolling and heat treatment of different duration at temperature of 350–500 °C was studied with the help of metallographic analysis. The changes on the boundaries of composite components were investigated depending on influence of increased temperature taking into account standard temperature of the reactor core and its possible short-time change, provided by technological incidents in reactor work.

The analysis of structure of composites was carried out on templates cut out along the thickness normal to the boundaries of layers joining. Mass transfer from one metal into other on the boundaries of composite components with interlayers was studied by a method of micro X-ray spectrum analysis in parallel with the metallographic analysis.

Analysis of diffusion changes on the boundaries of joining of layers after heat treatment showed the presence of the following factors:

- absence of visible transient zones on the boundaries of joining in Zr1–Nb–Cu–08Kh18N10T composite after all modes of heat treatment;
- presence of a thin (2–3 μm) transient layer with increased microhardness in separate places on V–Ni boundary in Zr1Nb–V–Ni–08Kh18N10T composites after annealing at 500 °C during 10 h. Approximate chemical composition of this layer — 13 wt.% V and 87 wt.% Ni — was determined by micro X-ray spectrum analysis. An increase of holding time up to 50 h resulted in formation of solid V–Ni intermetallic layer of up to 5 μm thickness. Appearance of the brittle intermetallic phase reduces the strength of joining of layers and provides failure of the composite along the joining boundary;
- thin transient zone of 2–3 μm width, which at continuous annealing does not have significant increase, was found on Zr–Nb boundary in Zr1Nb–Nb–08Kh18N10T composite after annealing at 500 °C during 10, 30 and 50 h;
- there were no intermetallic phases in Zr1Nb–Ni–08Kh18N10T composite on the boundaries of their components after annealing at 500 °C during 10 h. Transient zones from the side of nickel of up to 4 μm and from the side of zirconium of up to 15 μm, which belong to solid solution type, appear after annealing during 50 h and holding.

One of the most important problems occurring during development of new materials is their corrosion resistance in operating environment. A method of autoclaving under temperature and pressure, simulating conditions of operation of the materials in reactors [5], is used for evaluation of the quality of elements of structures from zirconium alloys during manufacture under industrial conditions.

It is quite difficult to use traditional methods for determination of the level of corrosion resistance of metals and alloys on weight increments of the samples per unit of area in a course of specified testing time for layered composites. Materials included in content of composites (three or four) differ by various oxidation resistance in corrosive medium. It is virtually impossible to determine contribution of each of them into general weight increment of the samples. Therefore, the following factors are the criterion for evaluation of corrosion properties of composites in autoclaving:

- state of the surface of microsection (homogeneity, density and color of films);
- presence or absence of the defects in the form of cracks, corrosion, accumulation of products of corrosion on the boundaries of joining of composite components;
- mechanical properties (tearing strength of layers) of the samples after different time of holding in the autoclave under working conditions.

As can be seen from Figure 1, *a, b*, there is a transient zone of width up to 3 μm on the boundary between zirconium and nickel on the surface of Zr1Nb–Ni–08Kh18N10T before and after corrosion treatment. Its width increases up to 5–7 μm after corrosion tests

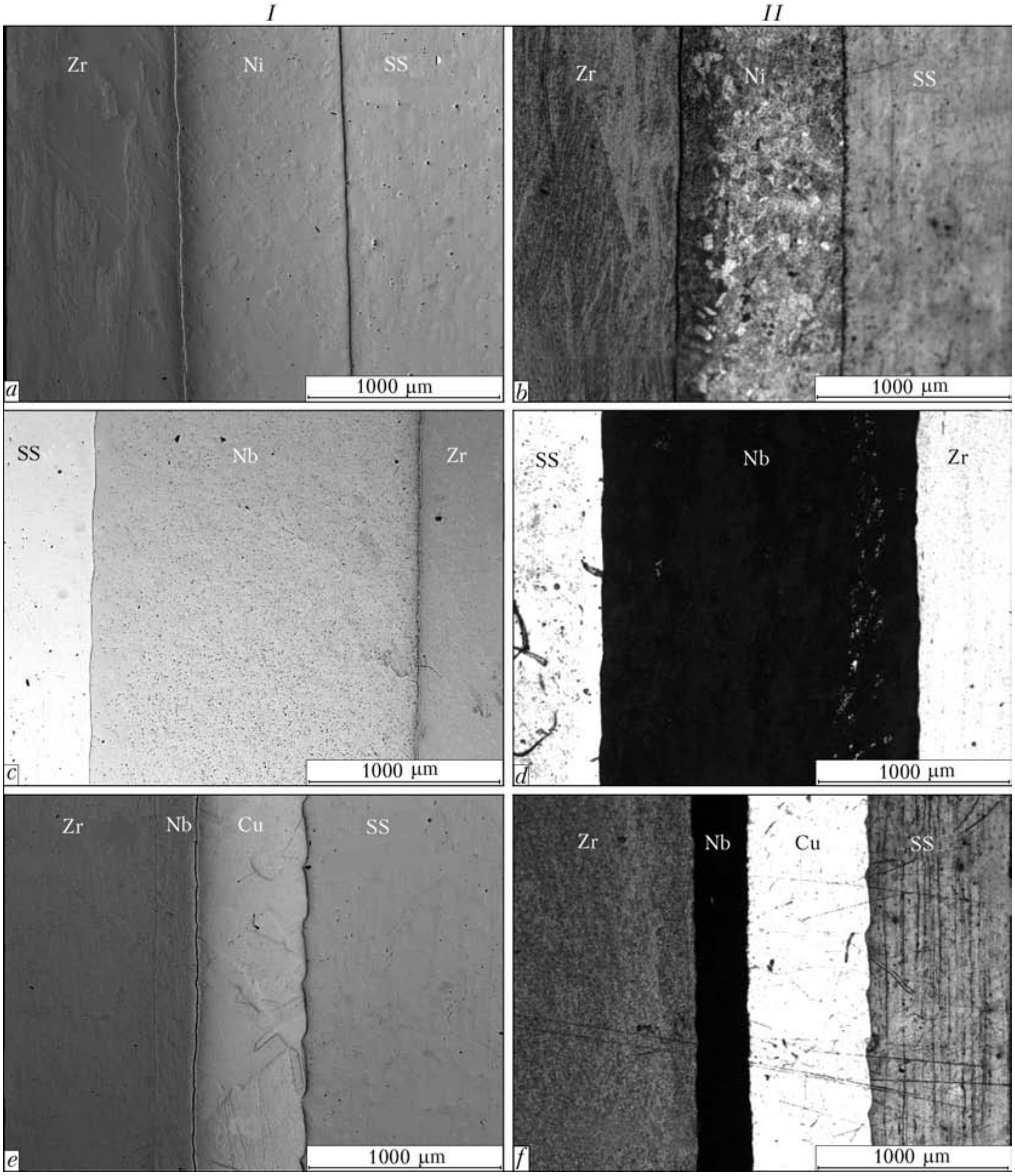

Figure 1. Microsections of Zr1Nb–Ni–08Kh18N10T (*a, b*), Zr1Nb–Nb–08Kh18N10T (*c, d*) and Zr1Nb–Nb–Cu–08Kh18N10T (*e, f*) composites in the initial state (after rolling) (*I*) and after corrosion treatment during 100 h (*II*)

during 1000 h. With increase of the time of corrosion tests insignificant pitting corrosion appears on nickel surface, and grain structure is formed in nickel and zirconium. There are no significant changes on the surface of SS except for light oxidation of the areas situated around precipitates of residual ferrite and carbides, giving these areas bluish color.

In the initial state of composite Zr1Nb–Nb–08Kh18N10T no intermediate transient zones on the boundary between composite components were found before and after corrosion treatment (Figure 1, *c, d*). Gray dense oxide film occurs on the surface of niobium interlayer after 50 h of corrosion tests and light areas appear in separate places, apparently, not yet covered by oxide layer. More dark areas appear on gray oxide film and it takes spotted nature after 100 h of tests. The main composite components did not suffer from significant changes except the appearance of thin oxide layers as in other compositions. The niobium interlayer gets significant thinning due to surface corrosion after 500 h of tests, it becomes loose, delamination in its surface sections from a free surface contacting with liquid corrosion medium, takes place. A stair of height up to 30–40 μm forms between zirconium and niobium due to difference in the rate of corrosion between these metals. A character of observed changes is kept after 1000 h of tests, the stair between zirconium and niobium increases up to 70 μm. The surface of niobium remains spotted with light and dark grey areas that can be an effect of formation of two or three types of oxides – NbO, NbO_2 and Nb_2O_5.

An appearance of intermediate zones on the boundaries of the components was not determined in Zr1Nb–Nb–Cu–08Kh18N10T composite (Figure 1, *e,*

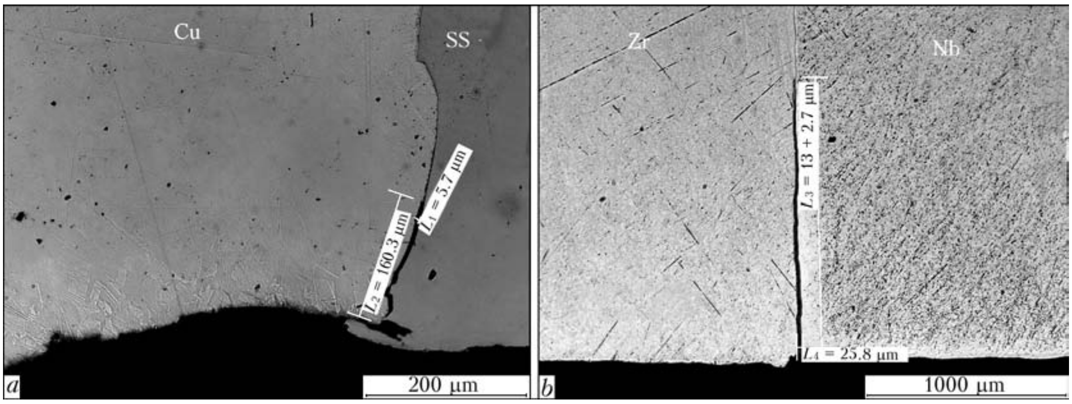

Figure 2. Microstructures with delamination after corrosion tests during 1000 h of composites Zr1Nb–Nb–Cu–08Kh18N10T on Cu–SS boundary (L_1 — delamination width, L_2 — its length) (*a*) and Zr1Nb–Nb–08Kh18N10T on Zr–Nb boundary (L_3 — delamination length, L_4 — its width) (*b*)

f) in the initial state (after rolling) and after corrosion tests. Structure is revealed in copper interlayer after 500 and 1000 h of corrosion tests. Copper surface remains light without significant oxidation marks after 1000 h and the pits of etching of dislocation structure were determined inside the copper coarse grains. The changes of the surface of niobium interlayer after corrosion tests are similar to that of composite Zr1Nb–Nb–08Kh18N10T.

For more detailed study of the changes in the state of boundaries of composites after corrosion tests the microsections were remanufactured from surface of which a layer damaged by corrosion was removed. At that, a layer of 5–7 µm thickness was determined in composition Zr1Nb–Nb–08Kh18N10T on Zr–Nb boundary after 500 h of corrosion tests and after 1000 h its thickness increased up to 11–12 µm. Discontinuities in the form of narrow crack are formed in the separate places with free surface of the sample on Zr–Nb boundary.

Very thin delaminations of a length from several micrometers up to 350 µm were formed in Zr1Nb–Nb–Cu–08Kh18N10T composite on the boundary of copper with steel after 500 and 1000 h of corrosion tests from both sides of free surfaces of microsections. The delaminations over 1000 µm length and up to 25 µm width were formed on Zr–Nb boundary in Zr1Nb–Nb–08Kh18N10T composite after 1000 h of tests. Found delaminations on Cu–SS and Zr–Nb boundaries (Figure 2), obviously, are the result of formation of galvanic couples from materials having different electrode potentials (Zr–Nb and Cu–SS) [9].

Mechanical tests of samples of the composites in the initial state (after rolling) and after corrosion treatment were carried out at temperature of 20 °C. As can be seen from Figure 3, all compositions in the initial state are characterized by significantly high strength properties. The greatest values of tensile strength (445–465 MPa) take place in composite Zr1Nb–Ni–08Kh18N10T. Failure of the samples occur along the intermediate interlayers.

Significant reduction in strength of the composites is observed after corrosion treatment. Thus, a tensile strength in composite Zr1Nb–Nb–08Kh18N10T after 1000 h of tests reduces from 340–350 (in the initial state) down to 100–110 MPa (after corrosion treatment) and from 390–410 down to 145–155 MPa, respectively, in composite Zr1Nb–Nb–Cu–08Kh18N10T. The data of metallographic analysis of fault samples indicate that the discontinuities in the form of cracks on the boundaries of interlayers with zirconium and steel are formed in the process of autoclaving as a result of electrochemical corrosion and stresses on the boundaries of composite components due to different coefficients of linear thermal expansion. The delamination occurs along perimeter of samples in the places of contact with corrosion medium that results in significant reduction of joints strength and premature failure of the composites.

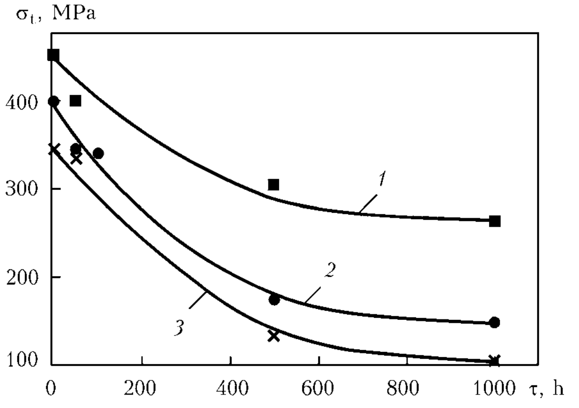

Figure 3. Dependence of tensile strength σ_t of Zr1Nb–Ni–08Kh18N10T (*1*), Zr1Nb–Nb–Cu–08Kh18N10T (*2*) and Zr1Nb–Nb–08Kh18N10T (*3*) composites on time τ of corrosion tests

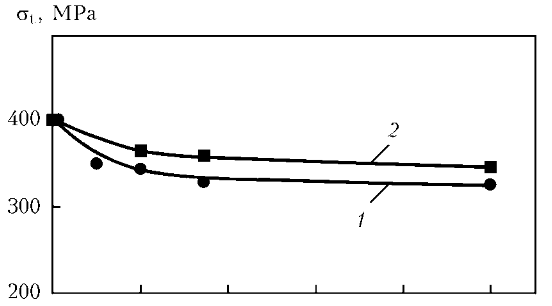

Figure 4. Dependence of tensile strength σ_t of Zr1Nb–Ni–08Kh18N10T (*1*) and Zr1Nb–08Kh18N10T (*2*) composites on bombardment dose D

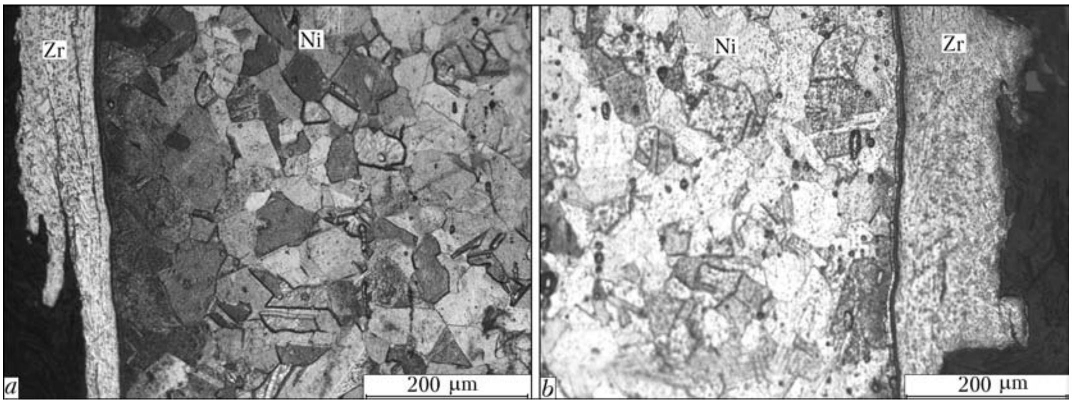

Figure 5. Microstructure of Zr1Nb–Ni–08Kh18N10T composite without (*a*) and after (*b*) bombardment by electrons of 10 MeV energy at D = $110\cdot10^{20}$ el/m^2

Reduction of strength of Zr1Nb–Ni–08Kh18N10T composite after corrosion tests during 500 and 1000 h is related, apparently, with an increase of width of transient zone (possibly, Zr_2Ni) on the boundary of zirconium with nickel. There were no defects in the form of porosities and delaminations on the boundaries of contact of composite components.

Composite Zr1Nb–Ni–08Kh18N10T was selected as the most perspective for further investigations of radiation resistance based on carried out analysis of studied composites and composite Zr1Nb with steel 08Kh18N10T without interlayer was takes for comparison.

Bombardment of the composites was carried out on the accelerator KUT-1 by electrons of 10MeV energy with bombardment dose which made $(3.3–330)\cdot10^{20}$ el/m^2. The influence of bombardment on mechanical properties of studied composites was evaluated after short-time tests at temperature of 20 °C with respect to maximum tearing strength of flat samples (Figure 4).

Investigation results showed that the tearing strength of layers for both composites reduces insignificantly and after dose of bombardment of $66\cdot10^{20}$ el/m^2 virtually does not change up to maximum dose $330\cdot10^{20}$ el/m^2. Maximum reduction in strength for both composites makes 15 %.

The character of composite failure is different depending on presence or absence of nickel interlayer. Thus, the failure in composite Zr1Nb–08Kh18N10T always occurs on the boundary of zirconium with steel and it takes place along zirconium component of the composite close to boundary with nickel (Figure 5) in the case of presence of nickel interlayer.

CONCLUSIONS

1. Physico-mechanical properties of composites Zr1Nb–Nb–08Kh18N10T, Zr1Nb–Ni–08Kh18N10T, Zr1Nb–Nb–Cu–08Kh18N10T and Zr1Nb–V–Ni–08Kh18N10T in the initial state (after rolling) as well as after temperature and corrosion tests were investigated. Composite Zr1Nb–Ni–08Kh18N10T has the highest value of strength after rolling (445–465 MPa).

2. Investigations of changes in the states of surface and strength of developed composites in corrosion medium, which simulates working conditions in WWER-1000 type reactors, were carried out. It is determined that the corrosion treatment results in significant reduction of strength of solid state joint of the composites being studied. The highest strength values (255–280 MPa) after 1000 h of corrosion tests were determined in composite Zr1Nb–Ni–08Kh18N10T.

3. Study of the influence of electron bombardment up to dose of $330\cdot10^{20}$ el/m^2 on strength properties of composite Zr1Nb–08Kh18N10T with and without nickel interlayer showed that the maximum reduction of tearing strength of layers for both composites makes up to 15 %.

4. Composite material Zr–SS with interlayer from nickel, which is differ by good corrosion resistance and preserves significantly high strength after influence of aggressive medium and bombardment, is the most perspective based on results of carried out tests for application as adapter elements for dissimilar metal joints in reactor structures.

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