

Formation of Titanium Interlayer by Vacuum Arc Deposition to Increase the Durability of Titanium Nitride Coatings under Thermal Cycling Conditions

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Abstract—It is found that the formation of a titanium interlayer between a zirconium alloy doped with niobium (Zr–1% Nb) and a magnetron-sputtered titanium nitride coating by means of cathodic vacuum arc increases the adhesion strength of titanium nitride. Titanium nitride coatings have a NaCl-type cubic lattice and are mainly oriented parallel to the (100) plane. Upon thermal cycling in the temperature range of 20–800°C, the structure of the titanium interlayer transforms from α phase to β phase. Ti–TiN coatings are stable upon thermal cycling in the temperature range of 20–800°C. The deposition of a titanium interlayer does not increase the hydrogen permeability of titanium nitride.

Keywords: vacuum arc deposition, magnetron sputtering, titanium nitride, hydrogen permeability, rate of absorption, thermal cycling

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INTRODUCTION

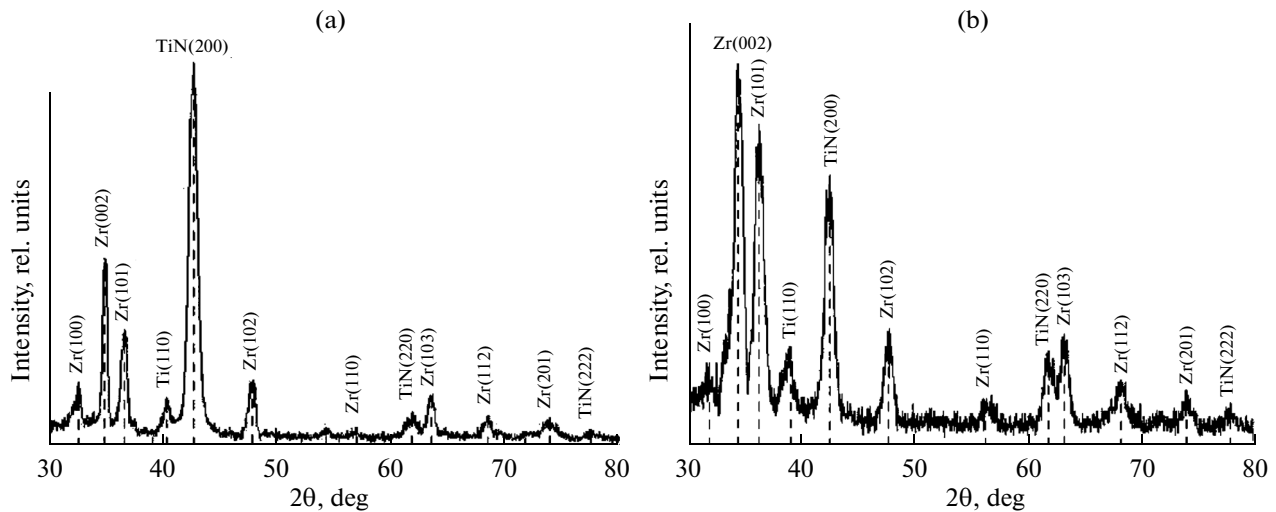
Zirconium alloys (Zr–1% Nb and Zr–2.5% Nb) are currently widely used as structural materials in the core of nuclear water–water energetic reactors (WWER) and high-power channel-type reactors (RBMK). Zirconium alloys become brittle upon contact with hydrogen-containing media, which causes degradation of their mechanical properties [1–5]. The use of zirconium alloys in the core of nuclear reactors should ensure the necessary protection of these alloys from corrosion, hydrogenation, and fretting wear. Vacuum ion-plasma coatings of transition metal nitrides are promising for the protection of zirconium alloys from hydrogen corrosion [6]. It is known that titanium nitride has high hardness and thermal and erosion resistance, which favorably affects the wear resistance of the coating [7]. It has been shown that TiN and Ti–TiN coatings formed by vacuum ion-plasma methods significantly lower the rate of hydrogen permeation through membranes of nickel and stainless steel [8, 9]. Thin films of titanium nitride deposited onto the cladding of fuel rods, made of NT-9 and MA957 alloys, considerably increase their mechanical strength and heat resistance, and also form a diffusion barrier for the penetration of nuclear fuel deeper into the rod cladding [10]. The formation of an oxide film on the surface of titanium nitride further enhances its corrosion resistance [11]. Previously, the rate of hydrogen absorption by titanium nitride coatings obtained by reactive magnetron sputtering at

different ratios of gases (N_2/Ar) depending on the thickness of the titanium nitride layer was investigated [12].

One of the most important tasks in the development of the technology of the application of titanium nitride coatings lies in ensuring good adhesion of the coating, including under thermal-cycling conditions. Differences in the temperature coefficients of expansion of the coating and substrate materials under these conditions may lead to destruction of the coating and, consequently, to a variety of disasters. For example, titanium nitride coatings on zirconium alloys, deposited by magnetron sputtering, are not stable during thermal cycling. In this paper, the problem of stability of the coating under thermal cycling is solved by creating an intermediate titanium layer by vacuum arc deposition between a Zr–1% Nb zirconium alloy and a titanium nitride coating.

MATERIALS AND METHODS

In the study, we used polished samples of Zr–1% Nb zirconium alloy, 20 mm in diameter and 0.5 mm in thickness. The average roughness of the samples after treatment was 0.12–0.14 μm . Titanium interlayers and the titanium nitride protective coating were obtained by cathodic vacuum-arc (CVA) deposition and magnetron sputtering (dcMS) using a Raduga Spektr setup of the Department of General Physics at Tomsk Polytechnic University. To implement the CVA method, a vacuum-arc evaporator with a plasma filter (developed by us [13, 14]) is used in the setup. The limiting residual pressure in the chamber was



X-ray diffraction patterns of a Ti–TiN coating on a substrate of Zr–1% Nb zirconium alloy (a) before and (b) after thermal cycling.

2.5×10^{-3} Pa. The sample surface was cleaned directly in the chamber of the setup by an argon ion beam with an energy of 1.5 keV at a beam current of 0.35 A.

The operation mode of the vacuum-arc evaporator upon deposition of the titanium interlayer was as follows: the discharge current (arc) was 110 A; the pulse negative potential bias at the substrate was 150 V; the pulse-repetition rate was 100 kHz; the maximum pulse current was 3A; and argon pressure in the chamber was 2×10^{-1} Pa. Titanium VT1-00 (99.9%) was used as the cathode.

Titanium nitride coatings were deposited by reactive magnetron sputtering at a gas ratio of $N_2 : Ar = 3 : 1$, pressure in the chamber of 1.54×10^{-1} Pa, and a discharge current and voltage of 4 A and 550 V, respectively. The deposition time was 30 min; a target of titanium (purity of 99.99%) was used.

The samples were saturated with hydrogen using the Sieverts method for 60 min at a pressure of $P = 2$ atm and temperature of $T = 350^\circ\text{C}$; the heating rate of the furnace was $6^\circ\text{C}/\text{min}$. The temperature of hydrogenation corresponded to the working conditions of the cladding of zirconium fuel rods in nuclear reactors.

The hydrogen permeability of the coatings was examined using a Gas Reaction Controller automated complex [15]. X-ray diffraction analysis of the coatings was performed using a Shimadzu XRD-7000 installation ($\text{Cu}K_\alpha$ radiation) at a voltage of 40 kV and a current of 30 mA with a fixed angle of incidence of $\theta = 3^\circ$. The thickness of the resulting coatings was

determined by analyzing a spherical cross section using a Calotest CAT-S-0000 instrument [16]. The adhesive strength of the coatings was measured by scratching with the use of a Micro Scratch Tester MST-S-AX-0000 device [17].

RESULTS AND DISCUSSION

It is known that the thermal-expansion coefficient of titanium takes an intermediate value between the corresponding coefficients for zirconium and titanium nitride. Furthermore, the method of cathodic vacuum-arc deposition is characterized by a higher energy of deposited particles, leading to the formation of dense coatings with high adhesive strength [18]. Thus, titanium is a joining metal in the substrate–interlayer–coating system. It seems obvious that this will promote equalization of the coefficients of thermal expansion between the substrate and the coating and improve the adhesion and thermal stability of the coating.

A titanium nitride coating with a thickness of 1.54 mm was applied by the procedure developed in [12]. The samples were subject to thermal cycling in a water-cooled vacuum oven with a variable heating rate. The limiting residual pressure in the chamber was $(6\text{--}7) \times 10^{-3}$ Pa. The heating and cooling rates were 200 and $\sim 2000^\circ\text{C}/\text{min}$, respectively. There were three cycles of heating and cooling of the samples of Zr–1% Nb zirconium alloy coated with TiN and Ti–TiN. After complete cooling, the samples were removed from the vacuum furnace. After thermal cycling, the surface of the sample without a titanium interlayer was comprised of portions of delaminated coating and there were cracks formed during heat treatment, which is not observed for the sample with a titanium interlayer.

The results of X-ray diffraction analysis of the samples before and after thermal cycling are presented in the figure. Assessment of the X-ray diffraction patterns

Table 1. Adhesion strength of TiN and Ti–TiN coatings

| Sample | Before thermal cycling | After thermal cycling |
|-------------------|------------------------|-----------------------|
| Zr–1% Nb + TiN | 7.7 ± 0.5 N | 4.4 ± 0.6 N |
| Zr–1% Nb + Ti–TiN | 9.8 ± 0.5 N | 9.9 ± 0.3 N |

Table 2. Rates of hydrogen absorption by samples coated with TiN and Ti–TiN

| Sample | Zr–1% Nb + TiN | Zr–1% Nb + Ti–TiN |
|--|----------------|-------------------|
| Rate of hydrogen absorption, $\times 10^{-4}$ cm ³ H ₂ /(s cm ²) | 1.75 | 1.64 |

using the ICDD database proved the presence of phases of titanium nitride (no. 38-1420), zirconium (no. 5-0665), and titanium in the α (no. 44-1294) and β (no. 1-074-7075) modifications. It is seen from the diffraction patterns that the coating of titanium nitride has a NaCl-type cubic lattice. The crystallites are mainly oriented along the (100) plane parallel to the substrate, which is preferable as the minimum surface energy is required [19]. As a result of thermal cycling, structural transformation of the titanium-interlayer α phase to the β phase occurs, followed by stabilization of the latter. The stabilization of β -phase titanium proceeds due to abrupt cooling (hardening) of the sample.

Before and after thermal cycling, three measurements of the adhesive strength of the coatings were performed for each sample by scratching the surface with an initial load of 0.01 N and an indenter load rate of 20 N/min. The measurement results are shown in Table 1. It is seen that with the titanium-interlayer formation, the adhesion strength of the titanium nitride coating increases from 7.7 to 9.8 N. After three cycles of heating to 800°C and cooling, the adhesive strength of the titanium nitride coatings without an interlayer drastically decreases to 4.4 N, which leads to local delamination of the coating. For the samples of zirconium alloy coated with Ti–TiN, the adhesion strength, at any rate, does not change.

After thermal cycling, the samples with a titanium interlayer were exposed to hydrogenation from gas atmosphere at $T = 350^\circ\text{C}$ and $P_0 = 2$ atm for $t = 60$ min. A decrease in the hydrogen pressure in the chamber upon saturation indicates that the samples absorb hydrogen. The slope of the pressure-time curves measured during hydrogenation characterizes the intensity of hydrogen absorption. The rate of hydrogen absorption is calculated according to equation

$$q = \frac{V}{tS} \ln\left(\frac{P}{P_0}\right), \quad (1)$$

where V is the chamber volume (175 cm³), t is the time of hydrogenation, S is the effective surface area of the samples, and P and P_0 are the final and the initial hydrogen pressure in the chamber.

The TiN-coated samples without an interlayer were not subjected to hydrogen saturation after thermal cycling because the continuity of the coating was violated. The rates of hydrogen absorption, calculated by Eq. (1) for the Zr–1% Nb alloy with a TiN coating (before thermal cycling) and a Ti–TiN coating (after thermal cycling) are presented in Table 2. It is seen that after thermal cycling, the rate of hydrogen absorp-

tion by the sample with an interlayer is lower than for the sample without an interlayer, which indicates a slight decrease in the permeability of hydrogen. Thermal cycling of the samples with a titanium interlayer did not cause any discontinuities in the coating or deterioration of its protective properties. Thus, while maintaining adhesion strength, the Ti–TiN coatings deposited onto the surface of the Zr–1% Nb alloy are stable under conditions of thermal cycling up to a temperature of 800°C.

CONCLUSIONS

The deposition of a titanium interlayer with a thickness of ~ 1 μm and subsequent application of a titanium nitride coating with a thickness of 1.54 μm by the cathodic vacuum-arc method result in the formation of Ti–TiN coatings on zirconium alloys, stable in a temperature range of 20–800°C.

With the application of a titanium interlayer, the adhesion strength of the TiN coating increases from 7.7 to 9.8 N. Thermal cycling of the samples coated with Ti–TiN does not lead to deterioration of the adhesion characteristics. Moreover, the rate of hydrogen absorption by the Zr–1% Nb zirconium alloy with a TiN coating decreases in the presence of a titanium interlayer from 1.75×10^{-4} to 1.64×10^{-4} cm³ H₂/(s cm²).

Under thermal cycling in the temperature range of 20–800°C, the α phase of titanium transforms into the cubic β phase, and subsequent stabilization of the β phase is attained by abrupt cooling (hardening). Ti–TiN coatings can be used to protect zirconium alloys from hydrogen corrosion under operation at temperatures up to 800°C.

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