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On Enhancing the Thermal Stability of Metal Hydrides by Ion–Plasma Vacuum Magnetron Sputtering

V. I. Pavlenko, N. I. Cherkashina*, R. N. Yastrebinsky, and O. V. Demchenko

V. G. Shukhov Belgorod State Technical University, Belgorod, 308012 Russia

**e-mail: natalipv13@mail.ru*

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Abstract—The method of titanium-hydride pellet (THP) modification by the surface deposition of metal titanium with the ion–plasma vacuum magnetron sputtering is described in this paper. The surface microstructure of the initial samples is compared with that of samples with the deposited coating. Found to be practically the same along the surface, the thickness of the deposited layer equals approximately 275 nm. The interface between the deposited titanium and THP is visible over the entire recorded region. The spectra of the thermal desorption of hydrogen from the initial and titanium-coated samples are presented. The coating is shown to significantly increase the temperature of THP dissociation.

Keywords: vacuum plasma sputtering, titanium coating, thermal stability, surface microstructure

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INTRODUCTION

Materials capable of effective neutron and gamma-ray deceleration and capture are required for the biological shielding of nuclear reactors. Since the mass of hydrogen is almost equal to that of a neutron, and, consequently, the neutron energy loss attains its maximum in collisions with hydrogen nuclei, hydrogen-containing materials are employed for the deceleration of neutrons in nuclear reactors. However, their applicability for biological shielding is limited because of hydrogen's high volatility and the low thermal stability of applied hydrogen-containing materials (e.g. water or polymers).

Since a significant amount of hydrogen can be dissolved in a metal crystal lattice, metal hydrides are also employed in nuclear reactors for neutron deceleration. Titanium hydrides, including in pellet form, are most commonly used [1]. Titanium efficiently absorbs gamma rays and also features high stability and a small mass. To enhance the thermal stability of a titanium-hydride pellet (THP), a coating is created on its surface, which prevents hydrogen loss upon heating the composite material [2, 3].

In the present work it is proposed to use the ion–plasma vacuum magnetron deposition of metal titanium on a THP surface for a reduction in the hydrogen loss at high temperatures. Such materials, which demonstrate a number of peculiar features, are interesting as the object of basic research and can be applied for radiation-shielding systems in the nuclear power industry.

EXPERIMENTAL

THPs fabricated by JSC "VNIINM" as spherical grains according to the technical specification of JSC "NIKIET" were used in the study. The grains represented spherical particles 0.2–2.5 mm in diameter. The THPs were modified during the study by the deposition of metal titanium onto them. The coating was deposited using a QUADRA 500 TM vacuum facility which was equipped with an off-balance magnetron sputtering system. A planetary mechanism was situated at the center of the vacuum chamber, while the magnetron plasma sources were mounted along the perimeter. Argon was used as the plasma-forming gas. Before depositing the coating, debris was thoroughly removed from the pellets by their twenty-minute storage in an acetone-filled ultrasonic bath. After that the pellets were washed with ion-enriched water and dried by dehydrated nitrogen.

The metal titanium target was mounted on the magnetron facility. THP samples (VT 1-0 grade) were placed on the object stage in the vacuum chamber. The volume containing the samples was evacuated to a residual gas pressure of 9×10^{-3} Pa. By means of an automatic gas-supply device the working gas (argon) was fed to the volume until a pressure of 6×10^{-2} Pa was reached. The object stage began to turn, while the ion source was switched to the etching mode; the accelerating voltage and ion current were 2200 V and 110 mA, respectively. After that ion decontamination of the titanium-hydride surface was performed for 10 minutes. the micro-contaminants preventing the formation of strong bonds between atoms of the substrate

Main diffraction characteristics of the studied THP samples

No.	2θ, deg	Area under the peak, arb. u.	Reflection intensity (*I*), pulses/s	Reflection halfwidth, Å	Interplanar spacing (*d*), Å	% max.[a]
1	18.3	7.184	72	0.175	4.8478	1.52
2	31.5	11.414	91	0.195	2.8269	1.92
3	35.2	497.264	4736	0.25	2.5495	100
4	40.85	228.831	1248	0.33	2.209	26.35
5	53.5	3.204	67	0.1	1.7127	1.41

[a] % max. indicates the peak intensity in percent with regard to the maximum intensity. In this case, the maximum peak intensity corresponds to peak no. 3.

surface and atoms of the deposited coating were removed from the THP surface. Preliminary vacuum treatment of the THP surface is known to significantly improve the adhesion of the protective coating.

After completion of the preliminary treatment, a steady supply of 99.999% pure argon with a relative partial pressure of 0.22 Pa was established by means of a metered gas-supply device. The magnetron was switched on and set to the mode 500 V, 5 A. Given that the distance between the magnetron and THPs was 100 mm and that the object-table rotation rate equaled 18 rotations per minute, the sputtering time amounted to 30 minutes. Apart from rotation of the table, the pellets were also rotated so as to provide uniform deposition of the coating.

X-ray phase analysis was performed using the DRON-3 diffractometer (CuK_α radiation, Ni filter) according to the standard method. The tube voltage amounted to 20 kV, the anode current was 20 mA, and the detector rotation rate was 2.4 degrees per minute with 1° angular pitch. The measurement rate limit reached 1000–4000 pulses per second. Data analysis and preliminary processing was performed with PDWin software (DrWin, Qual) using the PDF JCPDS database (version 2.02 1999).

The surface microstructure of the initial and modified pellets was analyzed with a TESCAN MIRA 3 LMU high-resolution scanning electron microscope at the V. G. Shukhov Belgorod State Technical University High-Tech Center.

An STA 449 F1 Jupiter device for synchronous thermal analysis by the company NETZSCH was utilized to carry out the differential thermal analysis of the THPs. The temperature ranged from 20 to 800 °C during recording; the heating rate was 10 °C per minute. To analyze the initial THPs, a 3 g weighed portion of powder was used, while the properties of the modified pellets were studied by placing a single pellet into a crucible. Aluminum oxide was used as the reference material.

RESULTS AND DISCUSSION

To determine the THP composition X-ray phase analysis was performed. TiH_2 and $TiH_{1.7}$ were chosen as the structural analogues for identification of the X-ray diffraction pattern. General X-ray diffraction characteristics of the analyzed THPs are given in the table. The pellets were found to have a chemical composition similar to that of $TiH_{1.8}$ with 3.8 g/cm^3 density.

Primary data concerning the material state can be obtained by analyzing the X-ray spectra profiles. The presence of high and narrow diffraction peaks indicates that the material is well-crystallized and has a homogeneous crystal lattice. Being characterized by a set of peaks against a smooth background, such an X-ray diffraction pattern is typical for a polycrystal.

In depositing metal titanium onto the pellets, the surface structure and the shape of the inital THPs are significant. Surface analysis by means of scanning electron microscopy (SEM) is performed in the study (see Fig. 1). As a result, moderate porosity, irregularity (with predominantly cavities) and the existence of rather shallow longitudinal cracks were found to be typical of the analyzed surface (see Fig. 1b). The surface cracks are explained by stresses resulting from the difference between the specific volumes of the titanium and the hydride [4–6].

According to the results of the performed surface microstructure analysis, the pellets with deposited metal titanium coating were found to have a rougher surface in comparison with that of the pellets without the coating (see Fig. 2). The surface structure is granular, the grain size being 25–50 nm. The grains prove to be oriented in some surface areas, which indicates texturization of the deposited metal layer. Longitudinal cavities observed on the surface of the original THPs were not detected. The cavities seem to be "cured" due to their filling with metal titanium and crystal-lattice build-up.

To examine the structure of the coating and to determine its thickness, a cleavage was carried out on

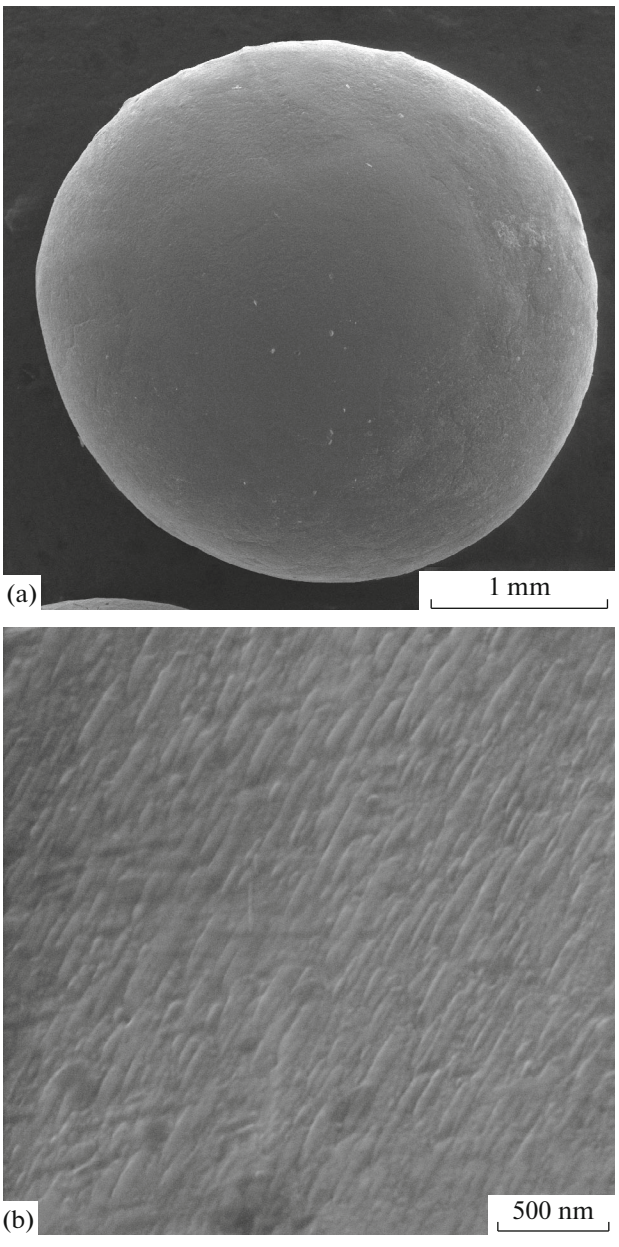

Fig. 1. SEM-image of the THP surface microstructure, obtained at (a) 80- and (b) 100000-fold magnification.

some THPs (see Fig. 3). The thickness of the deposited coating proved to be almost the same over the entire pellet surface and amounted to approximately 275 nm. The coating-to-THP interface is seen to be distinct over the recorded area. The deposited coating possesses a homogeneous structure and is tightly adjacent to the pellet surface. Since the chemical compositions of both the pellet and the coating include titanium, one can suggest good adhesion of the coating to the pellet surface due to the ability of titanium to embed into the pellet's crystal lattice.

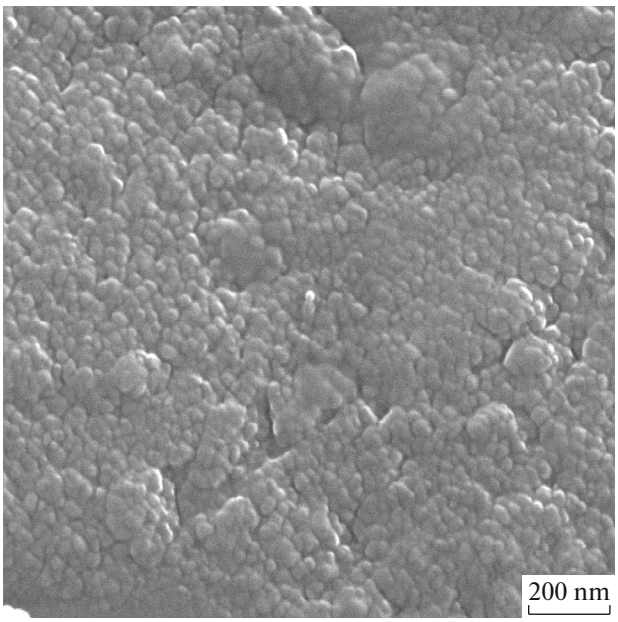

Fig. 2. SEM-image of the surface microstructure of a titanium-coated THP (200000-fold magnification).

The results of differential thermal analysis which evidence hydrogen desorption are shown in Fig. 4. Figure 4a corresponds to the initial THPs, while Fig. 4b corresponds to the THPs covered with metal titanium. According to the spectra given in Fig. 4, the thermal stability of the compared materials proves to be different in the temperature range from 450 to 800°C. The endothermic effect of decay is observed in the thermal desorption spectra of both examined materials. The decay of the initial THPs starts at 462°C and stops at 752°C. The maximal decay rate is achieved at 557°C. The endothermic effect is observed at temperatures above 500 °C and amounts to 120 kJ/mol, which is found to be in good agreement with known data [7].

Coating THP with metallic titanium significantly increases the starting temperature of the decay. In this case the decay begins at 615°C, while the temperature the decay stops at is 762°C. The latter barely differs from the results associated with the initial THPs. The hydrogen thermal-desorption peak from the coated THPs is attained at 694°C.

According to the data of differential thermal analysis, the peak of hydrogen thermal desorption from titanium-coated pellets, which corresponds to the start of hydrogen emission, proved to be shifted 153°C to higher temperatures in comparison with that of the initial THPs. One can also conclude that the hydrogen thermal-desorption peak corresponding to the maximum rate of hydrogen emission is shifted 152°C to higher temperatures for titanium-coated pellets in comparison with that of the initial THPs. Nevertheless, thermal desorption stops at practically the same

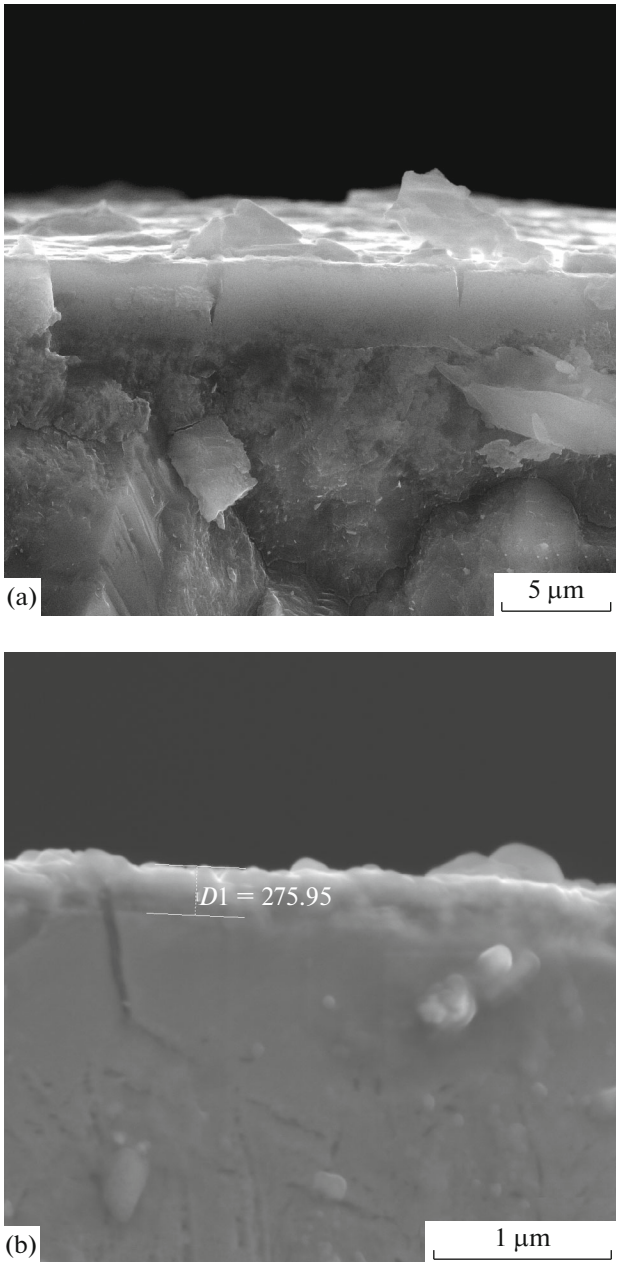

Fig. 3. SEM-image of the surface microstructure of a titanium-coated THP at (a) 10000- and (b) 80000-fold magnifications.

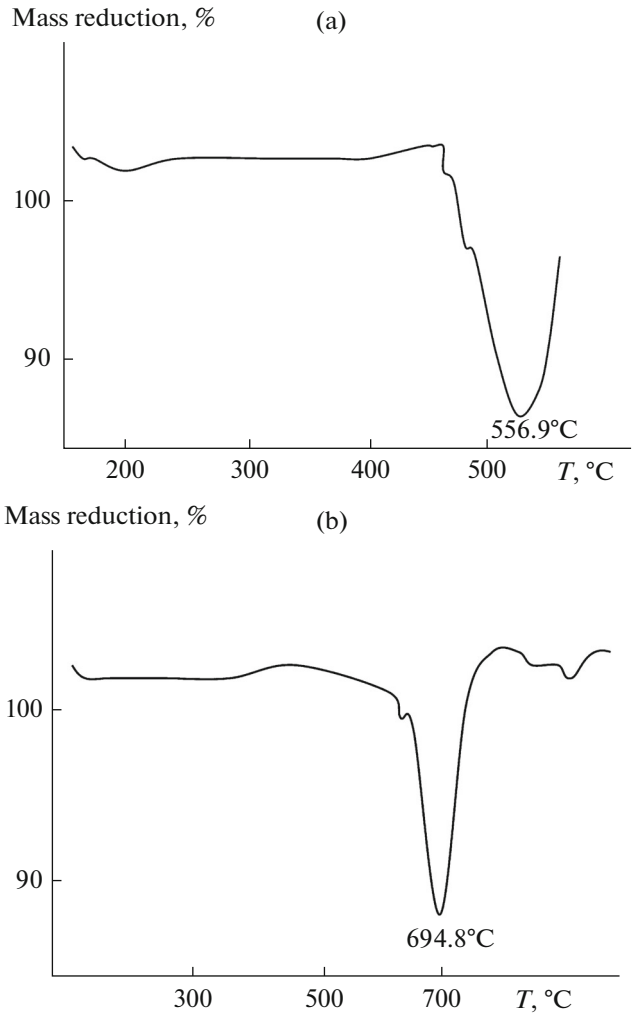

Fig. 4. Curves produced as a result of the differential thermal analysis of (a) the initial THP and (b) of the titanium-coated THP.

temperature (slightly above 750°C) both for the initial THPs and the titanium-coated pellets.

According to the data of the differential thermal analysis of titanium-coated THPs, the endothermic decay of titanium hydride can coincide in time with exothermic titanium oxidation by the oxygen admixed in inert carrier gas, which exhibits oxidation ability after partial hydrogen removal. As shown in Fig. 4 the exothermic process is distinctly expressed in the temperature range from 750 to 850°C.

CONCLUSIONS

Using the method of ion–plasma vacuum magnetron deposition on titanium-hydride pellets, a durable coating based on metal titanium has been produced. Analysis of the surface microstructure of the initial THPs has revealed moderate porosity, roughness (with cavities dominant) and the presence of deep cracks caused by a difference in the hydride and the metal-titanium specific volumes. Analysis of the surface microstructure of the titanium-coated pellets has shown that their surface is rougher in comparison with that of the uncoated THPs. The thickness of the deposited metal titanium remains almost the same all along the pellet surface and amounts to approximately 275 nm. The deposited coating has a homogeneous structure and adjoins tightly to the pellet surface.

The initial THPs and the ones modified with metal-titanium deposition were found to possess different thermal stabilities in the temperature range

from 450 to 800°C. According to the data of differential thermal analysis, the hydrogen thermal-desorption peak corresponding to the onset of hydrogen emission from the titanium-coated pellets is shifted 153°C to higher temperatures in comparison with that of the initial THPs.

The thin-film layer obtained via ion–plasma magnetron vacuum deposition can be utilized to produce a protective coating for THPs. Composite materials based on modified THPs can be applied in the nuclear-power industry as materials for biological shielding.

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REFERENCES

1. V. I. Pavlenko, O. D. Edamenko, N. I. Cherkashina, O. V. Kuprieva, and A. V. Noskov, J. Surf. Invest.: X-ray, Synchrotron Neutron Tech. **9** (3), 546 (2015).
2. O. V. Kuprieva, Vestn. Belgorod. Gos. Tekhnol. Univ. im. V. G. Shukhova, No. 5, 161 (2014).
3. V. I. Pavlenko, V. M. Nartsev, O. V. Kuprieva, Z. V. Pavlenko, and N. I. Cherkashina, J. Surf. Invest.: X-ray, Synchrotron Neutron Tech. **9** (5), 1022 (2015).
4. *Metal Hydrides,* Ed. by W. M. *Mueller*, J. P. Blackledge, and G. G. Libowitz (Academic Press, New York, London, 1968).
5. V. L. Arbuzov, V. B. Vykhodets, and A. G. Raspopova, Metally, No. 4, 148 (1995).
6. E. A. Yatsenko, E. B. Dzyuba, and N. V. Veropakha, Izv. S.-Peterb. Gos. Tekhnol. Inst. (Tekh. Univ.), No. 16 (42), 115 (2012).
7. *Physical Chemistry of Solid State. Collection of Works,* Ed. by B. Stalinskii (Khimiya, Moscow, 1972) [in Russian].

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