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DEUTERIUM RETENTION IN TiN AND CrN COATED Ti-6Al-4V ALLOY UNDER LOW-ENERGY GLOW DISCHARGE DEUTERIUM PLASMA EXPOSURE

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The influence of CrN and TiN coatings, deposited by cathodic arc evaporation, on deuterium permeation behavior in Ti-6Al-4V alloy was studied. Depth distribution profiles of deuterium were determined for both coated and uncoated Ti-6Al-4V samples following exposure to low-energy deuterium plasma to a fluence of $1 \cdot 10^{23}$ D/m^2 at room temperature. In the uncoated alloy, deuterium was found to redistribute throughout the bulk material, with permeation extending to the back side of the sample with respect to the irradiated surface. In contrast, deuterium permeation was limited to a negligible depth within the CrN and TiN coatings, demonstrating their excellent barrier performance.

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INTRODUCTION

In order to combat climate change, there is a global need for deep decarbonization, and all sectors that produce carbon dioxide (CO_2) must play a role. The good news is that there are solutions available today to enable reduction of the power sector's carbon emissions. In addition to solar, wind, and other renewable power sources, we have opportunities to reduce the carbon emissions from existing fossil fuel–based technologies, like gas turbine power plants. The gas turbine can operate on hydrogen and blends of hydrogen, and a future transition to the use of hydrogen as a zero-carbon gas turbine fuel may be possible.

A pure hydrogen environment is known to damage metal components including certain steels and titanium through different mechanisms including hydride formation, swelling, surface blistering, and embrittlement. One of the alloys types used for advanced gas turbine engines is Ti-6Al-4V. Titanium alloys have reasonable resistance to chemical attack, but hydrogen attack causes severe problems, such as loss of ductility and decreased material strength.

Since in most cases a single material cannot provide the required combination of mechanical robustness/strength and sufficient oxidization resistance, some of the gas turbine components are coated and/or internally cooled. However, before coatings can be used in gas turbine, it is necessary to understand the processes of hydrogen isotopes retention in these coatings and to determine the efficiency of hydrogen traps to bind hydrogen and preventing it from reaching cracking sites.

Commonly used hydrogenation tests of alloys and protective coatings are based on exposure of the samples to high-temperature water or steam ambient in autoclaves [1]. The disadvantage of these methods is a need for thousands of hours to make a conclusion about the resistance to hydrogenation of an investigated sample. More rapid hydrogenation techniques, such us gas-phase saturation according to the Sieverts method and electrochemical hydrogenation are known [2]. However, the conditions of both high-pressure hydrogen ambient in gas-phase saturation technique and low-temperature electrolyte environment in electrochemical hydrogenation method are much farther from conditions than water/steam ambient of the autoclave. The application of the accelerated hydrogenation method could be realized using a simple plasma device and it does not require high power consumption. It is shown that the characteristics of hydrogenation under the irradiation with 300…500 eV/at. ions of hydrogen plasma and under exposure to superheated steam are similar, but the hydrogen uptake under irradiation occurs hundreds of times faster than during the steam test. These circumstances allow suggesting the irradiation with hydrogen atoms and ions as an accelerated hydrogenation test of alloys and protective coatings [3].

The aim of our work was to study the deuterium retention in Ti-6Al-4V alloy in initial state and with TiN, CrN coatings deposited by ~~the~~ cathodic arc evaporation and exposed to low-energy deuterium plasma.

1. MATERIALS AND EXPERIMENTAL TECHNIQUE

Samples of titanium alloys Ti-6Al-4V, with chemical composition (wt.%) Al (5.3…6.8), V (3.5…5.3), Zr (0.30), Si (0.10), Fe (0.60), O (0.20), H (0.015), N (0.05), C (0.10), other impurities (0.30) and Ti (bal.) were studied. The samples had the following geometric parameters: disks with the diameter of 8 mm and thickness of ~1.9 mm.

A set of TiN, CrN coatings was formed using ion-plasma treatment of the samples on a "Bulat-6"-type apparatus at the initial pressure of $1 \cdot 10^{-3}$ Pa and operating nitrogen pressure of about 2 Pa. To improve the adhesion of the nitride layers, a thin metal (titanium or chromium) sublayer of 0.1 μm thickness was deposited on the titanium alloy surface in vacuum (0.001 Pa) at a bias voltage of -100 V. Negative bias voltages (U_b) of -50, -150, and -300 V were applied to the samples. The temperature of the samples did not exceed 450 °C. The thickness of the deposited coatings was 13…15 μm.

The Ti-6Al-4V alloy without and with TiN, CrN coatings was saturated with deuterium using glow gas-discharge plasma at 1000 V. The design and operating principle of the gas plasma source used for irradiation of

the samples is described in detail in [4]. The sample temperature was measured by the thermocouple and was (30±2.5) °C during saturation. The fluence was $1 \cdot 10^{23}$ D/m^2. The experimental ion flux and fluence were calculated from the measured ion currents and beam spot areas.

The implanted deuterium depth distribution was measured by means of the D (^{3}He, p)^{4}He nuclear reaction (NRA). The measurements were performed at room temperature using back scattering geometry. Deuterium depth profiles were extracted from the obtained data using "Helen" software [4, 5].

2. RESULTS AND DISCUSSION

2.1. DEUTERIUM PERMEATION BEHAVIOR IN UNCOATED Ti-6Al-4V ALLOY

To assess the effectiveness of the barrier effects of coatings, an initial examination was conducted on the permeation and accumulation of deuterium in uncoated Ti-6Al-4V alloy. Fig. 1 presents the experimentally measured energy dependence of proton yield from the D(^{3}He, p)^{4}He reaction, along with the calculated depth distribution profile of deuterium in Ti-6Al-4V alloy, which was saturated with deuterium using a glow discharge plasma at room temperature up to a fluence of $1 \cdot 10^{23}$ D/m^2. Energy spectrum of protons from the reaction D (^{3}He, p)^{4}He is shown in the insert. Measurements were taken 24 h after the sample saturation.

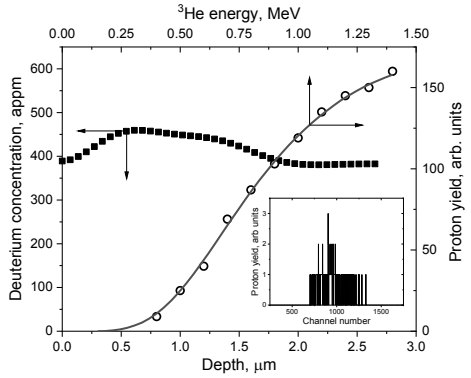

Fig. 1. Depth distribution profiles of deuterium in initial alloy Ti-6Al-4V saturated with deuterium using glow gas-discharge plasma at room temperatures to a fluence of $1 \cdot 10^{23}$ D/m^2. Energy spectrum of protons in the insert

Under deuterium plasma exposure, the calculated average projected range of D^+ ions with an energy of 500 eV was estimated to be ~10 nm. However, as illustrated in Fig. 1, deuterium is detected throughout the entire depth accessible to analyzing $^3He^+$ ions with an energy of 1.4 MeV (probe depth). The implanted deuterium is nearly uniformly distributed to a depth of 2.7 μm, with an average concentration of approximately 400 appm. Additional measurements conducted 120 h post-saturation revealed that the deuterium distribution profile remained largely unchanged in shape, although the concentration decreased by about 25%.

The Ti-6Al-4V alloy examined in this study is characterized by α + β structure [6]. Recent room-temperature investigations of hydrogen effects on this alloy have shown that the β-phase preferentially forms a solid solution with hydrogen due to its relatively high diffusion rate. This hydrogen uptake is accompanied by volumetric expansion, generating localized stress near the α/β interface. As a result, hydrogen tends to accumulate near this boundary, enabling gradual hydride growth along the interface [7]. Additionally, other studies have identified γ-TiH and δ-TiH_x as stable hydride phases at room temperature, with the structural characteristics of these hydrides being influenced by the localized occupancy of hydrogen atoms [8]. In our experiments, a high local concentration of deuterium in the near-surface layers of the sample during plasma exposure can promote hydride formation, thereby enhancing deuterium retention in this region.

Our previous studies on deuterium behavior in zirconium alloys showed that redistribution of deuterium occurred throughout the material bulk, extending to the backside of the sample relative to the irradiated surface [5]. This phenomenon was attributed to the high mobility of hydrogen and its isotopes in zirconium alloys. Given the apparent similarity between titanium and zirconium systems in terms of hydrogen-related behavior [9], a comparable mechanism can be expected for titanium alloy.

To evaluate deuterium permeation ability to greater depths, the first 0.4 mm of the Ti-6Al-4V sample, previously saturated with deuterium and stored at room temperature for 1200 h, was mechanically removed from the plasma-exposed side. Subsequent NRA analysis indicated the presence of deuterium at this 0.4 mm depth, with an average concentration of approximately 70 appm. Moreover, a notable concentration of deuterium (~50 appm) was also detected on the backside of the sample relative to the irradiated surface. Fig. 2 illustrates the experimentally measured deuterium profiles from the front side (after the removal of 0.4 mm) and the backside of the sample, as well as a linear interpolation of the gas concentration throughout the sample.

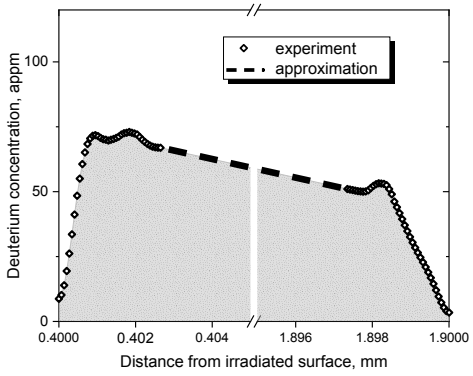

Fig. 2. Depth distribution profiles of deuterium at a depth of 0.4 mm from the plasma exposed side and at the back side of the Ti-6Al-4V sample 1200 h after saturation with deuterium

The sharp drop in deuterium concentration near both surfaces of the sample appears to be due to the effects of mechanical polishing prior to NRA analysis.

Considering a one-dimensional diffusion scenario, the diffusion distance (L) is proportional to the square root of both the diffusion time (t) and the diffusion coefficient (D): $L \approx (2Dt)^{1/2}$ The diffusion coefficient of hydrogen in Ti-6Al-4V exhibits an Arrhenius-type temperature dependence, $D = D_0 \times exp(-Q/RT)$, with activation energy Q = 32.80 kJ·mol^{-1} [10] and a

frequency factor $D_0 \approx 2 \cdot 10^{-3}$ cm^2·s^{-1} [11]. At the temperature of T = 300 K this would yield the hydrogen diffusion coefficient $D \approx 4 \cdot 10^{-9}$ cm^2·s^{-1}. Respectively, the estimated distance of deuterium transport over a period of 1200 h is approximately 1.86 mm, which correlates well with the thickness of the sample.

2.2. DEUTERIUM RETENTION IN TiN AND CrN COATED Ti-6Al-4V ALLOY

X-ray diffraction analysis has shown that single-phase textured cubic nitrides of TiN and CrN are formed in these coatings at bias voltages of -50 to -300 V [12]. The degree of microdeformation in the coatings decreases with increasing substrate bias voltage. At the same time, the crystallite size increases significantly (from D ≈ 26 nm to D ≈ 93 nm) for TiN coatings, and for CrN coatings, the crystallite size doesn't depend on bias changes and is equal to D ≈ 36 nm [12].

Fig. 3 shows the energy dependence of proton yield from the D (^{3}He, p)^{4}He reaction, and the calculated depth distribution profile of deuterium in CrN-coated Ti-6Al-4V alloy after exposure to deuterium glow discharge plasma at room temperature up to a fluence of $1 \cdot 10^{23}$ D/m^2. Measurements were taken 24 h after the sample saturation.

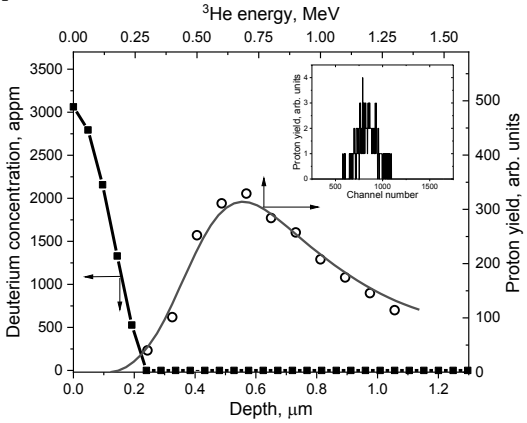

Fig. 3. Depth distribution profiles of deuterium in CrN-coated Ti-6Al-4V alloy after exposure to deuterium plasma to a fluence of $1 \cdot 10^{23}$ D/m^2. Energy spectrum of protons in the insert

The results of NRA analysis indicate that deuterium permeation into the material does not exceed 250 nm. In this study, the method of nuclear reactions in backscattering geometry, combined with the analysis of proton energy spectra, was employed due to its advantages in probing greater depths. However, the depth resolution of this approach is limited to 250 nm, which constrains the ability to accurately characterize the spatial distribution of deuterium in the near-surface region.

Virtually identical results were obtained in the study of deuterium permeation through all coatings studied in this work. Fig. 4 shows the depth distribution profiles of deuterium in CrN and TiN coatings deposited under varying applied bias voltages U_b.

Additional analysis performed after the irradiated samples were stored at room temperature for 120 h revealed no changes in the amount or distribution of deuterium, indicating the high efficiency of deuterium trapping in the near-surface region of the irradiated material.

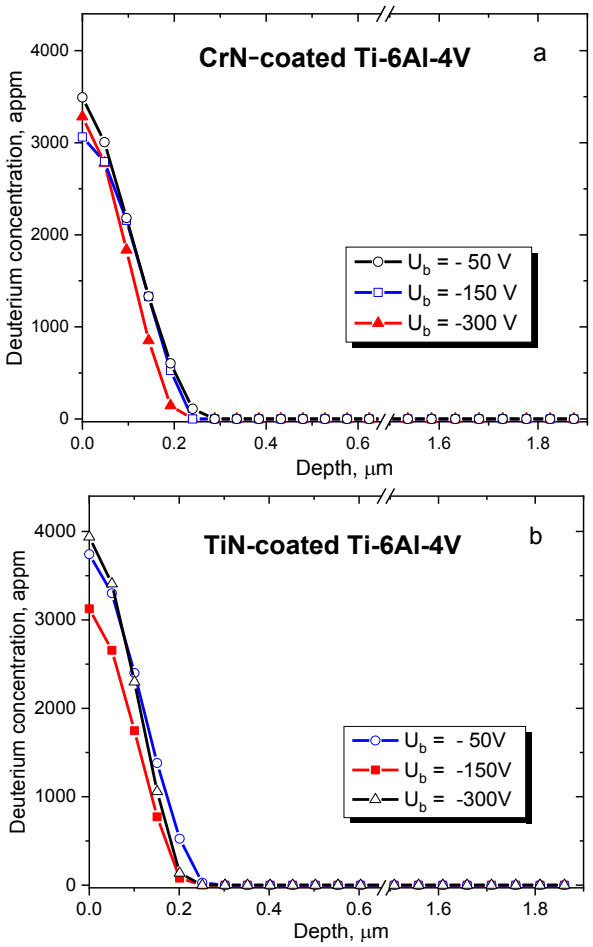

Fig. 4. Depth distribution profiles of deuterium in coatings CrN (a) and TiN (b) coatings on Ti-6Al-4V alloy saturated with deuterium using glow gas-discharge plasma at different substrate bias

Furthermore, no traces of deuterium were detected in the substrate material after mechanical removal of the coatings. These results demonstrate that the investigated coatings provide excellent resistance to deuterium permeation at room temperature.

Ceramic coatings, such as TiN and CrN, have received considerable attention due to their excellent mechanical properties and chemical inertness, particularly in harsh environments. These coatings have the potential to improve hydrogen permeation resistance by over two orders of magnitude, depending on factors such as the substrate material, coating composition, thickness, and compactness [13]. In particular, Tamura studied hydrogen permeation characteristics of TiN coated stainless steel and measured a 100 to 5000-fold reduction in permeation compared to uncoated substrate depending on the grain size of the coating, with the larger grain sizes showing higher hydrogen permeability [14].

In the context of hydrogen permeation, the effective permeability of materials is influenced by two critical parameters: the diffusion coefficient and solubility. Depending on the specific material properties and the method of hydrogen saturation, two different permeability mechanisms can be identified based on the mode of hydrogen transport: the diffusion-limited mode, in which bulk diffusion dominates in controlling kinetic processes, and the surface-limited mode, in which surface reactions dominate the transport dynamics.

In the present study, accelerated D^+ ions were implanted at a specific depth, bypassing surface-related processes such as physical adsorption and chemisorption. Consequently, surface phenomena do not affect the permeability, even though nitride coatings are generally characterized by low hydrogen adsorption efficiency. This suggests that the mechanism limiting hydrogen permeation is associated with the limited diffusion of hydrogen atoms within the bulk of the coating. Furthermore, the observed extent of deuterium permeation is extremely low, indicating negligible diffusional mobility of deuterium within the studied coatings at room temperature.

The existing literature lacks both calculated and experimentally measured Arrhenius-type temperature dependencies for the diffusion coefficients of hydrogen isotopes in TiN and CrN. Therefore, a comprehensive evaluation of the barrier performance of these coatings requires further investigation at elevated temperatures.

CONCLUSIONS

The deuterium permeation behavior in Ti-6Al-4V alloy, both in its uncoated state and with TiN and CrN coatings deposited by cathodic arc evaporation, was investigated following exposure to low-energy deuterium plasma at room temperature to a fluence of $1 \cdot 10^{23}$ D/m^2. The following conclusions were reached:

– In the uncoated Ti-6Al-4V alloy, significant redistribution of deuterium was observed throughout the bulk material (~1.9 mm), with permeation extending to the reverse side of the sample relative to the irradiated surface.

– In the coated samples, deuterium permeation was minimal, indicating negligible diffusional mobility of deuterium within the TiN and CrN coatings at room temperature. In addition, the depth of penetration and the concentration of accumulated deuterium in the coatings do not depend on the substrate bias voltage (in the range of -50 to -300 V) at which these coatings were deposited.

– The TiN and CrN coatings have the potential to serve as barriers, protecting the Ti-6Al-4V alloy from interaction with the hydrogen isotope deuterium.

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УТРИМАННЯ ДЕЙТЕРІЮ У СПЛАВІ Ti-6Al-4V З ПОКРИТТЯМ TiN ТА CrN ПІД ВПЛИВОМ НИЗЬКОЕНЕРГЕТИЧНОЇ ДЕЙТЕРІЄВОЇ ПЛАЗМИ ТЛІЮЧОГО РОЗРЯДУ

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Вивчено вплив покриттів CrN і TiN, нанесених методом катодного дугового випаровування, на поведінку дейтерієвого проникнення у сплаві Ti-6Al-4V. Профілі розподілу дейтерію за глибиною були визначені для зразків Ti-6Al-4V з покриттям і без покриття після опромінення низькоенергетичною дейтерієвою плазмою до дози $1 \cdot 10^{23}$ D/м^2 за кімнатної температури. У сплаві без покриття було виявлено, що дейтерій перерозподіляється по всьому об'єму матеріалу, причому проникнення поширюється на зворотний бік зразка по відношенню до опроміненої поверхні. На відміну від цього проникнення дейтерію було обмежене незначною глибиною в покриттях CrN і TiN, що демонструє їх високі бар'єрні характеристики.