Influence of concentration-time parameters on nitride coatings formation on VT6 titanium alloy and their stability during subsequent treatment

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Abstract. The possibility of using a titanium nitride coating as a «protective» layer against the penetration of hydrogen into VT6 titanium alloy semi-finished or finished products was shown in this article. It was found that the titanium nitride coating does not dissolve during high-temperature vacuum annealing and «isolates» sample sides from hydrogen penetration, which allows to form a linear gradient structure during subsequent thermal hydrogen treatment.

1. Introduction
Currently, the developments to increase military equipment lethality are constantly ongoing all over the world, so the improvement of armor protection materials with a higher weight strength and smaller size always remains a vital task [1, 2]. One of the main trends in this direction is the creation of materials with gradient structures. Such structures have a number of significant advantages over «classical» heterogeneous structures and provide increased impact strength, a slowed crack propagation rate, and high dynamic resistance. Various methods are used for such structure formation, such as local high-energy heating [3], intense plastic deformation [4, 5], hot deformation [6], surface chemical-thermal treatment [7], etc.

Titanium alloys are one of the most promising materials for armor protection, as they have higher strength compared to aluminum alloys (AMg5, V95, 1901 and others), lower density than classic steels (77, 44S, C85, SPS-43 and others), and also have less brittleness than ceramic materials based on oxides and carbides (Al2O3, SiC, B4C) [1, 8-10].

One of the technologies used to create a gradient structure in titanium alloys semi-finished products is thermal hydrogen treatment based on reversible hydrogen alloying [11-16]. However, to create the materials with increased dynamic resistance to directed high-speed loads it is necessary to transform the structure of one sample side only, which leads to a «one-way» changing gradient structure formation in the semi-finished product, i.e. when the structure over the semi-finished product cross section varies linearly from one surface to the opposite. In this case, the task arises of «isolating» the remaining sides of the semi-finished product from hydrogen penetration.

This work is a continuation of the studies conducted by the authors in this direction [17, 18]. It was shown in [17] that one of the methods of such «protection» is oxide layer formation on the surface during high-temperature treatment in an air atmosphere. Subsequent thermal hydrogen treatment allowed to create «one-sided» gradient structure in 12 mm-thick plate [18]. However, it was found that oxide films
effectively «protect» from penetration of up to 0.4% of hydrogen only, which limits the depth of its one-sided directed penetration [18]. Besides, the process of high-temperature oxidation leads to alpha layer formation with the depth of up to 250 μm and, therefore, subsequent machining for its removal is required. Thus, it is necessary to search for alternative protective coatings as, for example, nitride ones [19, 20, 21]. They practically do not form a diffusion transition zone, have strong adhesion to the surface, and therefore can be considered as one of the options for the «protection» of titanium semi-finished products during hydrogen alloying.

Therefore, the aim of this work was to study the effect of the temperature-concentration parameters of vacuum ion-plasma treatment on the formation of a nitride coating, its thickness and resistance to vacuum annealing and hydrogen penetration.

2. Materials and procedures

Investigations were performed on the 15×13×13mm samples cut from 13mm thick industrial manufactured hot-rolled plate made of VT6 titanium alloy.

Titanium nitride deposition was performed in Bulat-6 device. Vacuum annealing was carried out in a Vega-3M vacuum furnace. The thickness of the nitride coating was determined using ball-cratering method by Calotest device. The crater was grounded using a 25 mm ball at a speed of 900 rpm for 15 seconds. The measurement was carried out on six sides of the sample in five different places.

Addition of hydrogen was performed in Sieverts device in a molecular hydrogen atmosphere. The amount of added hydrogen was determined by weight gain with an accuracy of 0.0001 g.

Microstructures were investigated using a Cals Zeiss Axio-Observer.A1m graphic microscope at up to x600 magnification. Light-field mode in air atmosphere was used. The hydrogen penetration depth was determined on metallographic specimens by the change of microhardness. Each measurement line contained 50 measures with 100 μm gap between. The Vickers microhardness was measured on a MicroMet 5101 device with a diamond tetrahedral pyramid and a load of 50 g. The results were processed using MicroHardness software.

3. Results and discussion

At the first stage of work, VT6 alloy samples were subjected to vacuum ion-plasma treatment to form an «insulating» nitride coating. To ensure the best adhesion strength of the coating and the minimum acceptable level of its residual stresses, the deposition process was carried out at a temperature of 400°C. The deposition time was 5, 20 and 30 minutes.

A visual inspection of the samples after deposition showed that, regardless of the deposition time, a continuous defect-free golden/yellow-colored coating forms on all samples (Fig. 1).

Figure 1. Samples exterior after application of titanium nitride at a temperature of 400°C for 5 (a), 20 (b) and 30 (c) minutes.

The studies showed that nitrides are formed on five sample sides have the same thickness over the entire area, while one side of sample have a fairly thinner layer, which determined by sample orientation to the electrode during deposition process (Fig. 2, side 1). Therefore, nitride coating was removed from
this particular side before the subsequent thermal hydrogen treatment. An increase in the deposition time from 5 to 30 minutes leads to an increase of the coating thickness from 0.7 to 2.8 μm, respectively (Fig. 2).

**Figure 2.** Titanium nitride coating thickness, measured on 6 samples sides after coating deposition for 5 (a), 20 (b) and 30 (c) minutes.

At the next stage of work, to estimate the stability of nitride coatings during vacuum processing, all samples were subjected to vacuum annealing at a temperature of 800°C for 1 hour.

Visual inspection of the samples exterior and determination of the coating thickness (Fig. 3) showed that the color and thickness of the nitride coating practically do not differ from the «initial» state under all deposition conditions. Thus, studies have shown that nitride coatings formed after different deposition duration do not dissolve during the subsequent vacuum annealing.

**Figure 3.** Titanium nitride coating thickness, measured on 6 samples sides after coating deposition for 5 (a), 20 (b) and 30 (c) minutes and subsequent vacuum annealing at 800°C for 1 hour.

The «insulating» properties of the nitride coating formed on the samples deposition for after 30 minutes with subsequent hydrogen addition were studied at the final stage of this work. Sample side with the thinnest coating depth was subjected to mechanical treatment to remove the coating before the
beginning of the hydrogen addition. Based on studies [13, 16] and taking into account the specifics of one-sided hydrogen alloying, 0.4% hydrogen addition was carried out at a temperature of 800°C. Accelerated cooling was carried out immediately after completion of the hydrogen absorption process to ensure its inhomogeneous distribution over the sample cross section.

Metallographic studies showed that almost single-phase $\beta$-structure with a small amount of $\alpha''$-martensite forms in the sample from the «coating-free side» (Fig. 4 a). Since almost all of the hydrogen is concentrated in the sample surface layer due to specific of hydrogen absorption, the structure is not transformed over the entire cross section, but only to a certain depth. As you move farther from the surface layers, a gradual decrease in the amount of the $\beta$-phase and martensite and an increase in the amount of the $\alpha$-phase are observed (Fig. 4 b) due to a decrease in the amount of hydrogen. At a depth of 5000 $\mu$m, the structure no longer differs from the «initial» annealed state (Fig. 4 c).

![Figure 4](image)

**Figure 4.** Microstructure of VT6 alloy sample at a distance of 1000 (a), 4500 (b) and 5000 (c) $\mu$m from the surface of «coating-free» side after hydrogen addition

According to the microhardness distribution, it was found that the depth of the transformed structure is about 4500 $\mu$m. The structure analysis from the direction of «nitride coating isolated» sample side showed that already at a 100 $\mu$m depth from the sample surface the structure practically does not differ from the initial «annealed» state, which indicates the absence of the hydrogen penetration through the titanium nitride layer (Fig. 5).

![Figure 5](image)

**Figure 5.** The structure of a VT6 alloy sample after hydrogen alloying at a 100$\mu$m distance from the surface of «titanium nitride coating isolated» side.

### 4. Conclusions

Thus, it was found that the nitride coating formed at a temperature of 400°C during the vacuum ion-plasma treatment can be used as a method of «isolating» the semi-finished product or product individual sides from hydrogen penetration during subsequent hydrogen addition to create a «linear» gradient structure.
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