Oxide films resistance to hydrogen penetration in VT6 titanium alloy

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Abstract. The ability of hydrogen to penetrate through the oxide film formed during air-atmosphere annealing at elevated temperatures on VT6 titanium alloy samples was studied in this paper. It was investigated that oxide film prevents the penetration of up to 0.4 wt.% hydrogen. It was shown that it is possible to change the depth of hydrogen penetration and the surface layer structure by varying the amount of added hydrogen. It was determined that the formation of a finely dispersed surface structure after the thermal hydrogen treatment allows to increase the surface hardness by 8-10 HRC, compared to the center of material.

1. Introduction

Armor weight reduction while maintaining a high level of its working properties has been a major field of research in the area of vehicles anti-impact protection [1-3]. This is because the most popular IV+ protection class armor must be applied on such vehicles while preserving its possibility of safe movement on public roads [4]. One of the ways to solve the existing problem is usage of much lighter titanium alloys instead of steels [6, 7]. There are hundreds of industrially manufactured Russian and international titanium alloys known at this moment [8]. Therefore, to choose the most acceptable of these alloys, and to develop the processing technology aimed to increase their dynamic stability are relevant. Such materials must contain a hard surface layers and a ductile bulk, which is necessary for the deformation of the damaging element and the greater impact energy absorption [6, 9-11]. This could be achieved by creating layered composite materials [12,13], materials with multilayer «sandwich-type» structures [14,15] or gradient structured materials [16-18].

Gradient structures, which consist of gradual transition from one type of structure to another between the surface and the center of material, could be created using local heating with high-energy heat sources or by intense plastic deformation [16, 17]. In particular, a reversible hydrogen addition can be used to create gradient structures in titanium alloys [19]. However, when it comes to armored materials, it is necessary to modify the structure from one side only, i.e. to create a «one-way» or «linear» gradient structure. In this case, top priority task is to «isolate» the remaining sides of the semi-finished product from hydrogen penetration.

This work is a continuation of the research conducted by the authors in this direction [20-22]. In [20, 21], the temperature-time parameters of air atmosphere heat treatment were determined, which made it possible to form an oxide film on VT6 samples with high «insulating» properties against hydrogen penetration. It was shown [20-22], that it is possible to create a «one-way» or «linear» gradient structure in VT6 alloy samples using thermal hydrogen treatment.
Therefore, the aim of this work was to study the oxide film resistance to hydrogen penetration, as well as to determine the influence of hydrogen addition to VT6 alloy samples structure formation and its properties.

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.

Samples oxidation was performed in air atmosphere using SNOL-2.2.5.1.8/10-I3 furnaces. Vacuum annealing was performed in Vega-3M vacuum furnace. Addition of hydrogen up to 0.3-0.5 wt. % was performed in Sieverts device at β-area temperatures.

The amount of added hydrogen was determined by weight gain with an accuracy of 0.0001 g. The amount of residual hydrogen was determined by the spectral method on an ISP-51 spectrograph device with an electronic analytical attachment MORS-1/2048/PCI.

Microstructures were investigated using a Cals Zeiss Axio-Observer.A1m graphic microscope at up to x1000 magnification. Light-field mode in air atmosphere was used. The hydrogen penetration depth was determined on metallographic specimens by the change of microhardness. 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. Rockwell hardness was measured on a MacroMet 5100T device with a diamond cone and a load of 1500 MPa.

3. Results and discussion

The initial structure of the VT6 alloy plate is well worked and consists of β-phase and partially deformed lamellar β-grains, which corresponds to type 3 of 9-type standard scale [23] (fig. 1a). All samples were annealed at the β-area temperature, followed by slow cooling to room temperature to form a macrolaminal structure. The resulting structure is also uniform in cross section and is represented by large β-grains surrounded by a α-border with lamellar α-phase inside the β-grain collected in a colonies and corresponds to type 9of 9-type standard scale [23] (Figure 1b).

![Figure 1](image_url)

Figure 1. Microstructure of VT6 alloy plate in initial state (a) and after β-area temperature annealing (b).

The influence of one-sided hydrogen addition on the patterns of structure formation in surface layers was studied at the initial stages of work. All samples were preliminarily oxidated in an air atmosphere at a temperature of 90°C for 4 hours to form a protective oxide film. Then, before the beginning of the hydrogen addition, oxide and alpha layers were removed from one side of the sample by mechanical treatment.

It is known [24, 25] that the diffusion mobility of hydrogen atoms is much higher than that of the main alloying substitution elements. Therefore, it is possible to control the completeness of the \( \beta \rightarrow \alpha \)-transformation in the titanium alloys over the sample cross section by changing the amount of added hydrogen and the duration of hydrogen annealing. Besides, it was shown in previous studies [26], that
in order to convert a large lamellar (\(\alpha+\beta\))-structure into a finely dispersed one, it is necessary to make sure that \(\beta \rightarrow \alpha \)-transformation is complete during hydrogen addition and the alloy structure is practically «\(\beta\)-phase only» after room temperature cooling with just a small amount of \(\alpha''\)-martesite up to 10%. Taking into account that addition of hydrogen lowers the polymorphic transition temperature, transformation of alloy structure to single \(\beta\)-phase state will occur at lower temperature. Besides, hydrogen mainly located in surface layers during one-sided hydrogen penetration and therefore less amount of hydrogen is sufficient to transform surface structure.

Hydrogen addition was performed at a temperature of 800°C with the amount of added hydrogen up to 0.3-0.6 wt. % in this work. To ensure an inhomogeneous distribution of hydrogen over the sample cross section, accelerated cooling was carried out immediately after the completion of the hydrogen absorption process.

Metallographic analysis of oxide-free samples side hydrogenated to 0.3% and 0.5% wt. showed that its structure is represented by \(\alpha''\)-martensite and \(\beta\)-phase (Figure 2a). Since almost all of hydrogen is concentrated in the surface layer due to specially created annealing conditions, the structure conversion does not occur over the entire sample cross section, but only to a certain depth. Amount of \(\alpha''\)-martensite decreases with distance from the surface layers increases, as well as the amount of \(\alpha\)-phase increases (Figure 2b).

At a distance of 3500 \(\mu\)m from the surface, the structure no longer differs from its annealed state and is represented by large \(\beta\)-grains surrounded by a \(\alpha\)-border with lamellar \(\alpha\)-phase inside the \(\beta\)-grain (Figure 2c).

![Figure 2. Microstructure of VT6 alloy samples after hydrogen addition up to 0.3 wt.% at the depth of 500 \(\mu\)m (a), 1500 \(\mu\)m and 3500 \(\mu\)m (c) from the oxide-free surface.](image)

![Figure 3. Microhardness distribution in VT6 alloy samples cross section after 900°C oxidation and hydrogen addition up to 0.3 (a) and 0.5wt% (b) from the direction of oxide-free surface.](image)
The microhardness was measured in the transverse direction. On each measurement line, 50 prints were set in increments of 100 μm. The depth where the microhardness began to change stepwise was taken as the boundary of the transformed structure layer. Analysis of microhardness distribution over sample cross section showed that transformed structure layer has uniform hardness of 350 HV0.05, while the hardness of bulk area varies from 340 to 450 HV0.05 due to its large lamellar morphology (Figure 3a). Thus, the thickness of the transformed layer is 1800 μm for samples with 0.3 wt. % of hydrogen and 2800 μm for the ones with 0.4 wt. % of hydrogen.

Analysis of structure transformation and microhardness distribution over samples cross section from the oxide film «isolated» sides (Figure 4a) showed that at the distance of 100 μm from surface the sample structure are no longer differs from its annealed state (before hydrogen treatment) (Figure 1b). This indicates a weak penetration of hydrogen through the oxide film.

![Figure 4](image)

**Figure 4.** Microstructure of VT6 alloy samples after hydrogen addition up to 0.3 wt.% at the depth of 100 μm from oxide film «isolated» sides (a) and its microhardness distribution (b).

Similar results were obtained on samples with 0.5 and 0.6 wt % of hydrogen added. The character of structure changes and microhardness distribution from the direction of oxide-free sample side is preserved. The depth of transformed layer with increasing amount of added hydrogen from 0.5 to 0.6 wt % gradually increases from 3000 to 4000μm, respectively.

However, as the hydrogen content increases, the formation of α”-martensite is observed in the structure (Figure 5a) from «isolated» by oxide film sides (Figure 5a). Moreover, the almost unchanged microhardness value of 300 HV0.05 is observed on a depth up to 2500 μm (Figure 5b). This indicates a partial loss of the oxide film "protective" properties. In addition, this may be the reason that the actual depth of the transformed structure layer from the direction of oxide-free sample side could be much larger during the hydrogen addition of 0.4 wt%.

![Figure 5](image)

**Figure 5.** Microstructure of VT6 alloy samples after hydrogen addition up to 0.5 wt.% at the depth of 500 μm from oxide film «isolated» sides (a) and its microhardness distribution (b).
At the final stage of work, vacuum annealing was carried out at a temperature of 625 °C to remove hydrogen to its safe amount and to form the final «linear» gradient structure. Preliminary hydrogenated to 0.3% and 0.4%wt samples were annealed.

The studies showed that in the process of gas removal during low-temperature vacuum annealing, the $\beta \rightarrow \alpha$-transformation develops and a dispersed structure forms in the surface layers of oxide-free sample side (Figure 6a). Structure becomes less disperse as distance from the surface increases (Figure 6b), and at a distance of 3500 μm from surface the structure no longer differs from its annealed state (Figure 6c).

![Microstructure](a) ![Microstructure](b) ![Microstructure](c)

**Figure 6.** Microstructure over cross section of preliminary hydrogenated up to 0.3 wt.% VT6 alloy samples after subsequent low-temperature vacuum annealing at a distance of 500μm (a), 2000μm (b) and 3000 μm (c) from oxide-free surface.

Analysis of microhardness distribution over sample cross section showed that the depth of transformed layer together with transition zone is 2300 and 2800μm after preliminary hydrogenation of 0.3% and 0.4 wt. %, respectively (Figure 7 and Figure 8). Macrohardness of surface layer with finely dispersed ($\alpha+\beta$)-structure is about 40 HRC, and the inner layer with unchanged large lamellar ($\alpha+\beta$)-structure is 32HRC.

![Macrostructure](a) ![Microhardness](b)

**Figure 7.** Macrostructure (a) and microhardness(b) distribution of preliminary hydrogenated up to 0.3 wt.%VT6 alloy samples after subsequent vacuum annealing at 625°C from the direction of oxide-free surface.
Figure 8. Macrostructure (a) and microhardness (b) distribution of preliminary hydrogenated up to 0.4 wt.% VT6 alloy samples after subsequent vacuum annealing at 625°C from the direction of oxide-free surface.

4. Conclusions

Studies have shown that the thermal hydrogen treatment of VT6 alloy samples with 5 of 6 sides «isolated» by oxide film allows to create a «one-way» or «linear» gradient structure that changes from finely dispersed on one side to a large lamellar on the opposite. It is shown that with an increase in amount of added hydrogen from 0.3 to 0.6 wt%, an increase in the depth of the transformed layer is observed from 1800 to 4000 μm, respectively. It was established that the oxide film formed during oxidation at 900°C effectively protects from hydrogen penetration up to 0.4wt.% only. It is also shown, that a dispersed structure formation in the surface layers allows to increase the hardness to 40 HRC. Thus, a «one-way» or «linear» gradient structure formed using thermal hydrogen treatment in VT6 alloy can provide increased impact strength and slowed crack proliferation rate in its samples.

5. References

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