Gradient structure formation in titanium alloys using thermohydrogen treatment technology

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Abstract. This paper shows the possibility of creating a “linear gradient” structure, which varies from finely dispersed globular grains to coarse lamellar ones over the cross section of a 13-mm semi-finished product of VT6 alloy, using the thermohydrogen treatment method. The formation of the oxide layer and the depth of oxygen penetration were studied depending on the heating temperature and duration of treatment. The oxide stability was assessed during subsequent annealing in vacuum. It was established that the only oxide film which provides protection from hydrogen penetration during hydrogenous annealing at 800 °C, was formed during heat treatment at 900°C for 4 hours.

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, 2]. This is promising field of study due to the fact that the most popular protection class is V and higher [3]. Also, regardless of the protection type, it should prevent penetration of the damaging elements into the vehicle cabin, while preserving the possibility of safe movement of this armored car on public roads [4]. Therefore, the specific characteristics of the material used in this area are important [5]. One of the ways to solve the existing problem is usage of titanium alloys, which have already proven themselves as the good individual armor protection material [6, 7]. It is known [3, 5, 8, 9] that in order to increase the dynamic resistance of protection, it is necessary for the used material to combine a hard surface layers with a ductile bulk, which ensures greater absorption of impact energy. This could be achieved by creating multilayer “sandwich-type” structures in various materials (Figure 1 a) or using layered composite materials (Figure 1 b) [10-12]. There are also promising methods that aimed at creating gradient structures in metallic alloys, which consists of gradual transition from one type of structure to another between the surface and the center of material (Figure 1 c). For example, the authors of selected works [13–16] created gradient structures using intense plastic deformation or local heating with high-energy heat sources.

![Schematic image of multilayered “sandwich-type” materials](image)

**Figure 1.** Schematic image of multilayered “sandwich-type” materials (a) [10], layered composite materials (b) [12] and gradient structure materials (c) [14].
A thermohydrogen treatment, based on reversible hydrogen addition, can be used to create gradient structures in titanium alloys [16–18]. Due to the difference of diffusion mobility between the hydrogen atoms and the main alloying elements, thermal hydrogen treatment can be used not only for volumetric structure transformation (Figure 2 a, b) [17], but also for its surface transformation (Fig. 2 c) [18]. Moreover, the mechanical properties of the material are largely determined by the depth of the transformed zone, as well as by the morphology, and the size of the structural components [18].

![Figure 2](image.png)

**Figure 2.** Transformation of VT6 titanium alloy volumetrical lamellar-like structure (a) to volumetrical dispersed globular structure (b) and «mixed» gradient structure (c) using thermohydrogen treatment [19]

However, when it comes to armored materials, it is necessary to create a «linear» gradient structure (Fig. 3), i.e. when the structure changes occur from one surface to the opposite, and not simultaneously from all surfaces to the center (Figure 2 c) [18].

![Figure 3](image.png)

**Figure 3.** Schematic image of “linear” gradient structure.

Thus, it is necessary to create such conditions when the transformation of the structure due to hydrogen addition will occur only in one direction from the surface. Therefore, the aim of this work was to study the capability of providing a “one-way” hydrogenation in VT6 titanium alloy samples.

2. Materials and procedures

Investigations were performed for the 13 mm thick industrial manufactured hot-rolled plates made of VT6 titanium alloy.

Heat treatment was performed using SNOL-2.2,5.1.8/10-I3. Addition of hydrogen up to 0.4 and 0.6 wt. % was performed in pure molecular hydrogen environment of Sieverts device at β and (α+β)-area temperatures.

Quality of oxide film was visually tested. Hardness was measured according to Rockwell method using the BUEHLER Macromet 5100T device.

Microstructures was investigated in a light-field mode in air atmosphere using a Cals Zeiss Axio-Observer.A1m graphic microscope at x1000 magnification.

The value of added hydrogen during hydrogen annealing 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.
3. Results and discussion

It is known [17] that a structure with a lamellar morphology of particles has a higher impact strength. The initial structure of the VT6 alloy plate was of a mixed type: it consisted of small primary α-phase lamellar grains and more dispersed α+β-mix, located between them (Figure 4 a). To create an even (α+β)-structure in the semi-finished product, all samples were annealed in the β-area temperatures, followed by slow cooling to normal temperature. The resulting structure is uniform in cross section and is represented by the initial 80-100 µm β-grains, surrounded by α-border and 3-5 µm thick lamellar α-grains, located in the volume of β-grains. Hardness of the samples after the annealing was 31-33 HRC (Figure 4 b).

![Figure 4. Microstructure of VT6 alloy plate in initial (a) and annealed (b) state.](image)

To determine the optimal value of added hydrogen, which is necessary to completely transform the lamellar structure and to ensure a significant increase in hardness, volumetric hydrogen treatment was carried up to a concentration of 0.4% and 0.6% at temperatures of 800°C (β-area) and 700°C (α+β-area). After the completion of hydrogen adsorption, the samples were kept under equilibrium pressure of hydrogen for 3 hours to ensure its uniform volume distribution. The residual hydrogen content in the samples did not exceed 0.006 wt.%.

Studies have shown that if hydrogen annealing up to 0.4 wt.% is carried out at a temperature of the β-area with subsequent cooling at 1K/s speed to room temperature, a structure consisting of β-phase and α‴-martensite (Figure 5 a) is formed. Increasing the hydrogen percentage up to 0.6 leads to the formation of an almost single-phase structure of β-particles (Figure 5 b). Decreasing the temperature of thermohydrogen treatment to 700°C keeps the (α+β)-structure retained in the alloy, characterized by an increased volume fraction of β-phase in comparison with an alloy in its initial state (without hydrogen) (Figure 5c).

![Figure 5. Microstructure of VT6 alloy samples after volumetric hydrogen addition up to 0.4 wt.% (a) and 0.6 wt.% (b) at β-area temperature and up to 0.4 wt. % (c) at (α+β)-area temperature.](image)
During the subsequent gas removal process, the structure is transformed due to the development of \( \beta \rightarrow \alpha \)-transformation. Following investigations have shown that in the process of vacuum annealing at 625°C, the processes of nucleation of \( \alpha \)-phase particles prevail over the processes of their growth. Thus, the structure of samples preliminarily hydrogenated up to 0.4 wt.% at a \( \beta \)-region temperature is represented by thin lamellar \( \alpha \)-phase, which inherits the shape of martensite (Figure 6 a). The structure of samples hydrogenated to 0.6% after vacuum annealing is represented by dispersed particles of the \( \alpha \)-phase (Figure 6 b). Low-temperature vacuum annealing of the samples after hydrogenation in the (\( \alpha+\beta \))-area leads to the formation of a bimodal structure of the \( \alpha \)-phase, consisting of large lamellar grains of the primary \( \alpha \)-phase, preserved in the structure during hydrogen addition, and dispersed particles of the secondary \( \alpha \)-phase, formed during gas removal process (Figure 6 c). The maximum hardness of 42 HRC provided by a structure with a dispersed \( \alpha \)-phase, while thin lamellar morphology structure provides slightly lower hardness (40-41HRC). Test samples with a bimodal structure have the lowest hardness of 37-39HRC.

![Figure 6. Microstructure of preliminary hydrogenated up to 0.4 wt.% (a) and 0.6 wt.% (b) at \( \beta \)-area temperature and up to 0.4 wt. % (c) at \( \alpha+\beta \)-area temperature VT6 alloy samples after subsequent low-temperature vacuum annealing.](image)

Further investigations showed that it is possible to change the morphology and size of the structural components of the VT6 alloy over a wide range by changing the temperature and percentage parameters of thermohydrogen treatment.

Since the main alloying elements diffusion in titanium alloys proceeds much slower than the hydrogen diffusion [19], there is a possibility to control the depth of hydrogen penetration and the completeness of \( \beta \rightarrow \alpha \)-transformation by changing the kinetic parameters of the thermohydrogen treatment. It was investigated that to obtain the maximum hardness after vacuum annealing, the alloy structure must contain \( \beta \)-phase particles only after the preliminary thermohydrogen treatment. Hence, the alloy should contain at least 0.6 wt.% of hydrogen. It was calculated that to provide at least 0.6 wt.% of hydrogen in the surface layers, the volumetric amount of introduced hydrogen should be around 0.3-0.4 wt. %.

During surface «linear» gradient structure creation the transformation of the structure due to hydrogen addition must be occured only in one direction from the surface. In this case the main task is to protect all sides of semi-finished product from hydrogen penetration but one. It is known that a thin oxide film formed on the surface of titanium prevents the penetration of hydrogen, but it dissolves when heated in vacuum [19]. Therefore, at the next stage of this study, the kinetics of dissolution of oxide films was studied during processing in vacuum. The samples were subjected to oxidation in an air atmosphere in the temperature range from 600 to 900°C for 1-4 hours. Visual inspection of the samples after oxidation at various temperatures for 4 hours showed that a dense oxide film forms on their surface (Fig. 7). The thickness of which, together with the alpha layer, decreases from 150 \( \mu \)m after treatment at 900 ° C to 20 \( \mu \)m at 600°C (Table 1). Reducing the exposure time from 4 hours to 1 hour at heating temperatures of 800-900° C also leads to the formation of oxide films firmly adhered to the surface. In this case oxide film thickness almost half as thin (Table 1).
Figure 7. VT6 alloy samples exterior after air atmosphere oxidation at 900°C (a) and 600°C (b) for 4 hours, as well as at 900°C for 1 hour (c).

Table 1. Oxide film thickness after air atmosphere oxidation depending on temperature and exposure time.

| Temperature | 900°C | 900°C | 900°C | 800°C | 700°C | 600°C |
|-------------|-------|-------|-------|-------|-------|-------|
| Duration    | 4 hours | 2 hours | 1 hour | 4 hours | 4 hours | 4 hours |
| Thickness, μm | 130 | 120 | 70 | 100 | 20 | 20 |
| After 800°C, 1 hour vacuum annealing | | | | | | |
| Thickness, μm | 250 | 170 | 100 | 120 | 100 | 100 |

The resistance of the oxide films on the samples surface during subsequent processing in vacuum was investigated. Since the maximum temperature of the thermohydrogen treatment is 800°C, the same temperature of vacuum annealing was chosen to evaluate the stability of the oxide.

It was found that vacuum annealing at 800°C allows to completely preserve the oxide film formed during 900°C isothermal exposure for 4 hours (Figure 8 a), while oxide films formed during 800 and 700°C isothermal treatment are partially dissolves during the same method of processing in vacuum. Oxide films formed during 600°C isothermal exposure are completely dissolving in vacuum (Figure 8 b). Exposure time decreasing also leads to a partial dissolution of the oxide film (Figure 8 c). In the process of vacuum annealing, oxygen diffuses deeper into the sample. Thus, the thickest and the most stable oxide layer is observed in samples which was preliminary annealed at 900°C for 4 hours (Table 1).

Figure 8. VT6 alloy samples exterior after air atmosphere oxidation at 900°C (a) and 600°C (b) during 4 hour exposure and at 900°C during 1 hour exposure (c), with subsequent 1-hour long high-temperature vacuum annealing.
At the final stage, the “protective” properties of the oxide film formed at a temperature of 900°C for 4 hours during thermal hydrogen treatment were investigated. Oxide film from one side of the sample was mechanically removed for further comparison of oxide protective ability. Thermohydrogen treatment up to 0.4% of hydrogen was carried out at a temperature of 900°C. In order to exclude a distribution of hydrogen over the cross-section of the samples, their cooling was carried out immediately after the completion of the hydrogen absorption process. To conduct a comparative analysis of thermal hydrogen treatment, samples not protected by an oxide film were also subjected.

Studies have shown that during hydrogen annealing, almost all of the hydrogen is concentrated in the surface layer of the sample; therefore, the structure is not transformed in the entire volume of sample, but only in the surface layer. The structure of the transformed layer is represented by $\alpha''$-martensite and $\beta$-phase (Figure 9 a). At a distance of 4000 $\mu$m from the surface, the structure no longer differs from its initial state (before hydrogen adsorption) (Figure 9 b). Investigation of structures from the other three sides («isolated» by the oxide film) showed that already at a distance of 100 $\mu$m from the surface it is represented by $\alpha$- and $\beta$-phases, which indicates a significantly lower hydrogen values (Figure 9 c).

![](image1)

**Figure 9.** Microstructure of VT6 alloy samples after 900°C oxidation and thermohydrogen treatment up to 0.4% of hydrogen at the $\beta$-phase area temperatures 1500 $\mu$m (a) and 4000 $\mu$m (b) from the oxide-free surface and 100 $\mu$m (c) from surface with the oxide film.

Microstructure analysis of a oxide-free sample showed that the depth of hydrogen penetration during the treatment from all sides is approximately the same and averages 2000 $\mu$m (Figure 10).

![](image2)

**Figure 10.** Microstructure of VT6 alloy oxide-free samples after thermohydrogen treatment at the depth of 1000 (a) $\mu$m and 2500 (b) $\mu$m from surface.
Subsequent low-temperature vacuum annealing makes it possible to completely transform the lamellar structure in the surface layers oxide-free side to the dispersed one, while maintaining it practically unchanged from the other three sides, which was «protected by oxide film» (Figure 11). The hardness of the 2800 μm transformed layer with a finely dispersed (α+β)-grains is about 39 HRC (Figure 11 a). Dispersion degree of the structural components is decreasing with the distance from surface (Figure 11 b). Structure became almost identical to initial (before hydrogen addition) state at a depth of 4000 μm (Figure 11 c). The hardness of such layers is about 34 HRC.

![Figure 11](image1.png)

**Figure 11.** Microstructure of VT6 alloy samples after oxidation at 900°C for 4 hours and thermohydrogen treatment at a depth of 1500 μm (a), 2800 μm (b) and 4000 μm (c) from oxide-free surface direction.

4. Conclusions

It was investigated that 250 μm oxide film formed during high-temperature treatment can be used to «protect» particular side of semi-finished or finished product from hydrogen penetration during thermohydrogen treatment. This can also be used to create the «linear» gradient structure, which changes from dispersed globular to coarse lamellar one over the cross-section of such products.

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