Structural features of the hydride phase formation in nanostructured α-titanium

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Abstract. Features of structurally-phase transformations in nanostructured and coarse grained (recrystallized) titanium in process of diffusion saturation by hydrogen in a wide interval of temperatures are studied.

1. Introduction

Nowadays titanium and its alloys [1] are the most popular metal materials used worldwide in production of medical implants. And intentional alloying is the traditional way to achieve the complex of necessary mechanical properties in such kinds of materials. As a rule, the most common alloying elements in the titanium alloys, such as Al, V, Mo, Ni, Nb, etc. are harmful or even toxic for living organisms. This can also be referred to a famous titanium alloy Ti-6Al-4V (ВТ6 in Russian terminology, Grade 5 alloy – its international analogue) that is widely used as a material for medical implants. However, a high level of toxicity of V has been recently found in experiments for cells survival in biological fluids [2]. There is a number of confirmations that Al can cause Alzheimer's disease and lead to bone softening (a systematic disease that is characterized by the lack of bone tissue mineralization) [3-5]. These drawbacks are not found in the nanostructured non-alloying titanium that has been got with the method of mechanical-thermal treatment under special technological regime of plastic deformation (severe plastic deformation); so it has got structural characteristics after quasistatic and periodic loading at the level of BT6 alloy. The idea of severe plastic deformation (SPD) use for such a titanium preparation was proved in the articles earlier [1, 6, 7].

It is well known that the change of metals and alloys structure with the help of SPD can lead to the major modification of mechanic and other properties, as well as of SPD mechanisms [6, 8]. When we use this method to achieve the formation of submicrocrystalline structure (SMC) or nanostructured (NS) condition we can achieve tensile strength duplication of commercial pure titanium VT1-0 that due to its bio inertness is used in medicine as implant material.

It is known that the intensity of mechanical and other properties deterioration in medical metal materials, when in operation, depends heavily on interreacting with biological tissue and fluids. The increase of hydrogen concentration in implants can be the result of such an interreacting. When the concentration of hydrogen in metals with hcp lattice is high, there starts the formation of fragile hydride phases in the volume and on the boundaries of grains succeeded by the beginning and rise of cracks in the phase interface [9-14]. It is stated that hydrogen diffusion saturation of titanium alloys starts in the biological environments containing hydrogen ions, shown on the example of dental implants.
This leads to grain boundary destruction on the surface of the volumes as the result of hydrides formation over there. It has been published earlier in the articles that such a situation leads to preterm implant destruction when in operation [13,15]. Probably the origin of hydrogen embrittlement of titanium alloys used in medicine is grain boundary segregation of iron that is a foreign matter in titanium alloys of commercial pure. It is known that this chemical element stabilizes titanium \(\beta\)-phase, mainly on grain boundaries. We can also watch the release of intermetal combinations of Ti\(_x\)Fe types on the grain boundaries. This leads to the decrease of metal corrosion resistance because the particles of intermetallicides serve as the ways for activating hydrogen diffusion inside the metal. Intermetallicides of iron group interreact with hydrogen at room temperature. The diffusivity of hydrogen in titanium alloys within these characteristics increases greatly [15]. However, notwithstanding the characteristics mentioned above, titanium alloys are widely used in medicine [16-19].

2. Material and experimental procedures

The coarse grained (99, 99%) and commercial pure titanium VT1-0 (total concentration of foreign matters 0.283 wt. % (N – 0.003, C – 0.004, H – 0.0008, Fe – 0.12, O – 0.143, Al – 0.01, Si – 0.002)) in nanostructured (NS) and coarse grained (recrystallized) conditions were used to determine the effects of how the structure influences hydrogen absorption in a wide temperature range. NS condition was formed by the impact of plastic deformation in screw and lengthwise rolling combination [20]. The average size of grain and subgrain structured elements in NS condition is \(d \approx 0.2\) micrometer. Recrystallized alloy VT1-0 had the grain average size of \(d \approx 12\) micrometers, iodide titanium – \(d \approx 240\) micrometers. Microstructure and the bar chart of size distribution of grain and subgrain structured elements are shown on figure1.

Hydrogen diffusion saturation of titanium was performed on a special laboratory machine of high pressure (Siverts method) 60 ml. The sampling material was placed into the reactor-digester, then it was vacuumized to the residual pressure of \(~1\) Pa within 1 hour at different temperatures from 300 to 500 °C. After vacuum condition was achieved, we added hydrogen under the pressure of 2-2.5 Pa and shut off the heat. If there was no hydrogenation, the heat was resumed and it continued before the pressure in the system stopped falling down (2-10 hours). Temperature and time interval of hydrogen saturation was put together taking into account the necessity to maintain NS condition.

Titanium cut was used as an accelerator for hydrogenation temperature decrease and hydrogen absorption process increase. As it is known, the dissociation of the molecular hydrogen on the atomic one takes place on the free surface of such a titanium cut. In this case the molecular and atomic hydrogen mixture is formed near the contact place of titanium cut with the surface in the reactor-digester. We have to mention that the atomic hydrogen has got a high level of diffusion mobility in the metal crystal lattice. This lets us reduce the temperature of hydride formation beginning. The speed of dissociation also depends on gas pickup conditions (temperature, pressure). The decrease of hydrogen charging temperature is a major factor for experimentation in the research of regularity of hydrogen influence on the NS materials structurally-phase condition, as it helps to maintain this condition.

All the works, preceding the hydrogen diffusion saturation of titanium, were performed in argon atmosphere in a dry box with the controlled inert atmosphere of M.Braun company (Germany). Highpurity hydrogen (99.9999%) from a metal hydride accumulator on the basis of LaNi\(_5\) was used for hydration.

The structure of hydride phases was identified with the help of gas-volumetric, chemical (CHNS/O elementary analyzer «Vario Micro Cube») and X-ray phase analyses. Thermal analysis was performed with the use of synchronic TG-DTA/DSC (Netzsch STA 409 Luxxx) in argon atmosphere (the heating rate of 10 °C/min).

Structural research was made on a scanning electron microscope Quanta 600 FEG with the field emission and in a transmission electron microscope Tecnai. The samples were prepared with the help of mechanic grinding-polishing installations LaboPol-5 (Struers), electropolishing of the sample surface was made on LectroPol-5 (Struers) installation in 60 ml HClO\(_4\) + 600 ml CH\(_3\)OH + 360 ml butylglycol solution at a temperature of \(+5\) °C and voltage of 23 V.
3. Results and discussion

Commercial pure titanium VT1-0 in its nanostructured and coarse grained (recrystallized) conditions (the average size of a grain and subgrain mixture is 0.2 and 12 micrometers respectively) and coarse grained iodide titanium (the grain size is 240 micrometers) (figure 1) were used to determine the effects of a structurally-phase condition on the process of hydrogen absorption by titanium. Hydrogen saturation of iodide and NS commercial pure titanium was made in one reactor-digester with a metal separating baffle, because the speed of titanium oxide layer (TiO\textsubscript{2}) in oxygen containing environments is very high and it is a strong barrier for hydrogen penetration into titanium matrix. It was discovered that initial structure of the sample influence the temperature of intensive hydrogen diffusion saturation of titanium.

As we can see on the graphs (figure 2) that have been obtained with the help of differential scanning calorimetry, there are differences in quantity and location of peaks for iodide and commercial pure titanium in its NS condition after diffusion saturation in hydrogen atmosphere. After hydrogen diffusion saturation of titanium at a temperature of 400 °C we can observe the peaks displacement to high temperature for NS titanium. Besides, there are additional peaks in the interval between 400 and 500 °C. This type of graph is similar to the one for titanium hydride in coarse grained (iodide) titanium [21]. The DSC curves, obtained for compact specimens, differ from the respective graphs for chipped samples. This is due to several processes. Firstly, heterogeneous processes located on the boundary line of solid/vapor influence seriously on specific surface value (surface area per unit volume), and when the latter rises, the processes proceed intensively. Secondly, the difference is in accelerating of gas pickup in the chipped samples. This happens due to the fact that hydride phase starts its formation in uncrystallized initial grain, but the grain has enough time to grow in the compact specimen under long term hydrogen saturation before the hydride phase begins. The article [21] shows a complex character of phase transformation of titanium hydride under annealing; this proves a possible structural change of the latter into one of its crystal modifications.

There is an explanation for the presence of two peaks on DSC curves of titanium dihydride, that correspond to nonequivalent position of hydrogen in hollows: one peak is in tetrahedral hollow, the other one is in octahedral [22]. For certain reasons [23] the additional peak formation, the second one exactly, is due to the presence of bet titanium hydride that transforms in to a cubic structure while heated. When the temperature of hydrogen diffusion saturation of NS titanium decreases the grain rate of growth goes down. As the result, hydride phase appears in a smaller grain. And when the temperature of hydrogenation is 400 °C the graph shows three distinct peaks. This indicates a double displacement of the structure or the presence of hydride mixture of different crystal lattice modification.
A high concentration of iron in VT1-0 alloy can influence the hydride formation kinetics significantly, as intermetallide TiFe serves an accelerator in the processes of titanium hydrogenation. Together with other mixtures that are often out of purposeful control and that are a part of VT1-0 alloy, iron can influence the morphological features of hydride phase formation in α-titanium.

To exclude the influence of foreign elements on hydride formation kinetics there was done a comparative research of commercial pure VT1-0 titanium diffusion saturation in nanostructured and coarse grained titanium that was formed as the result of recrystallization annealing from NS condition of this alloy.

Figure 3 shows the differences in DSC graphs for VT1-0 alloy after diffusion saturation in hydrogen atmosphere and for iodide titanium. Hydrogen charged samples in the form of titanium cut are characterized by a more complex nature of a graph with a number of endothermal peaks (figure 3a), a distinctive feature of NS condition is a less integral area between the peaks. It is important to note a complex way of DSC graphs, this can show structurally-phase transformations of hydride phase as well.

At hydrogen diffusion saturation of NS and coarse grained titanium (400 °C, 4 hours, 2MPa) the hydrogen concentration in the samples in the form of cuts is 0.54 and 0.84 % respectively. It is known that the plasticity of particle hardened metal alloys, for titanium alloys with hydride particles here (they are formed as the result of diffusive annealing in hydrogen atmosphere), directly depends on a form and character of hydrides distribution. Plasticity and impact hardness can increase at spherical and globular form of such particles under certain conditions. Long lamellar precipitate (here, hydrides) are a stress raiser that lead to decrease of material plasticity.

Morphological features of hydride formation in NS titanium are a significant result of our research.
Figure 4 shows that zigzag configuration hydrides are formed in such a material. Probably, this fact states that a significant role in hydride extraction in metals and alloys in SMK and NS condition belongs to residual inner stress that is common for such materials obtained under SPD [1]. A partial de-stress takes place in the process of formation and growth of zigzag configuration hydrides. The above described type of hydride extraction, called «hydride platelets» was observed earlier for some zirconia alloys (e.g: Zr702, (Hf 4.5%; Fe + Cr 0.2%; H 0.005%; N 0.025%; C 0.05%; O 0.16%) [25]. Titanium hydride extraction typical for pure titanium and some its alloys in coarse grained condition of test titanium alloy is observed on the grain boundaries [10, 14, 24].

Nanosized platelets extractions of 10 nm thick and 600 nm long that present inside a grain were discovered while investigating the structurally-phase condition of NS titanium through transmission electron microscopy (figure 4). The length of such extraction is limited with the size of grains. The given morphology of extractions is typical for hydride phase. It is known that depending on hydride phase type the lamellar precipitate are located on the boundaries and inside a grain [10]. Besides, particles of globular form were discovered (figure 4c), but due to their small size it is impossible to obtain their electron diffraction pattern.

The electron-diffraction pattern and dark-field figures, obtained from different sides of structure (b-longitudinal section, c- cross-section) of VT1-0 NS titanium after hydrogen saturation at the temperature of 400 °C is shown on figure 4b. This electron diffraction pattern shows an additional reflex circle that corresponds neither to hcp (α-titanium) nor to body centered cubic lattice (β-titanium). While identifying the pattern there were some difficulties because of a large number of reflexes that correspond to titanium α-matrix. However these reflexes prove the hydride extraction of TiH$_{1.971}$ and/ or TiH$_{1.924}$ type (TiH$_{1.971}$ (PDF – 2 №7-370, cubic system, space group I4/mmm), TiH$_{1.924}$ (PDF – 2 №25-982, cubic system, space group Fm3m)). Relative data of interplanar distance for hydride phases that have a cubic lattice as well as the combination of other factors didn't let determine the hydride phase structure precisely. Probably, TiH$_{1.924}$ hydride phase is presented by globular extractions, while TiH$_{1.971}$ has got sheetlike extractions. The presence of at least two crystal modifications of titanium hydride is confirmed indirectly by the presence of additional plateau and peaks on DSC graphs for NS condition.

4. Conclusion
Comparative examinations of structurally-phase transformations in nanostructured and coarse grained (recrystallized) titanium under its hydrogen diffusion saturation at a wide temperature interval are conducted. The differences in location and quantity of peaks on the graph are discovered, this proves more complex processes of hydride phase dissolution. The phase was formed after nanostructured titanium hydrogenation in comparison with the one fit with coarse grained (recrystallized) titanium. It is stated that hydride formation in nanostructured titanium takes place in the form of zigzag productions (by type of cracks formation and expansion) that look like the colonies of finely dispersed particles of submicrometer dimension compared to long particles typical for recrystallized condition.
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