Control of changes in the defect structure of titanium saturated with hydrogen

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Abstract. The hydrogenated samples of technical titanium were investigated using the EPA method and the measurements of the thermal electromotive force for these samples saturated with a different amount of hydrogen. The structure of the hydrogenated samples was studied by the X-ray diffraction method. The results have shown that the hydrogenated titanium structure starts changing at the same time, depending on the amount of added hydrogen. The intensity of the annihilation process increases with the increase in the hydrogen concentration in α-titanium up to the values of 4% wt and does not change up to the values of 5% wt (α + δ) - titanium. At the same time, the value of the thermal electromotive force decreases in this range of values. The annihilation intensity is stabilized for the values of 5% wt, and the value of the thermal electromotive force is increased. The inflection point for the thermal electromotive force versus the hydrogen concentration corresponds to the formation of δ - hydrides. The increase in the positron lifetime starts in the concentration range of 6-8% and moves to the stable level up to the concentrations of 21-22%. In this range, there is a transition from the (α + β) to the (α + δ) phase. The lifetime of positrons and the number of defects are increased, the value of the thermal electromotive force is reduced (up to the concentration of 24%), then there is a stabilization mode for all these parameters up to the values 32% wt.

1. Introduction

The development and improvement of the materials used in the nuclear industry or under extreme conditions should be controlled to meet such conditions. As a rule, these materials absorb hydrogen and become the hydride-forming ones [1]. In this case, hydrogen plays both a negative and positive role [2]. To control hydrogen, there is a need to use the methods providing the minimum radiation, the minimum toxic substances, and a wide temperature range. The development of control methods is closely connected with the study of physical processes accompanying the hydrogenation of metals [3]. Many of them, namely, the nuclear magnetic resonance, quasi-elastic neutron scattering, the Gorsky and Mössbauer effects require the complex equipment, and the received results are essentially dependent on the concentration gradient of added hydrogen, the hydrogenation method, and the form of the samples under study. Hydrogen is known to have a high diffusion mobility in metals and alloys and can form complex systems which include the vacancy-type defects, impurity atoms, dislocations, self interstitial atoms, as well as the grain boundaries [4]. Hydrogen interacts actively not only with the existing structural defects [1], but also causes the formation of a large number of new defects [5-8]. To create operational production control methods [1], there is a need to study the degassing processes [9], the nature and formation of hydrogen defects.

In the work we used the classical control methods for the measurement of eddy currents, the thermal electromotive force and electrical resistance [10-12], as well as the modern method of

electron-positron annihilation (EPA) [13]. The EPA method is quite effective for studying the dynamics of appearance, transformation and disappearance of defects in metals, and for determining the concentrations and dimentions of defects during the hydrogen saturation [5, 14].

The simultaneous use of different experimental techniques allows us to obtain the comprehensive quantitative and qualitative data on the structure and modification of the material and determine the defects in a wide temperature range for any hydrogenation method. This combination is useful not only for hydrogenation, but for degassing of hydrogenated samples.

2. Experiment

Preparation of samples. The commercially pure titanium samples with the linear dimensions of 30×30×1 mm were mechanically polished and annealed in vacuum at the temperature of 650 °C for 1 hour. The samples were saturated with hydrogen from the gaseous phase at a high pressure and temperature according to the Sieverts' method [12], using the automated complex "Gas Reaction Controller" [13, 14] (Advanced Materials Corporation). The samples were placed in a chamber that was evacuated to a pressure of 10^{-6} atm. Then the samples were heated in vacuum to a temperature of 600 °C at the heating rate of 4 °C/s. The slow rate of heating removes completely the desorbed gases during heating. Then the chamber was quickly filled with hydrogen to a pressure of 0.66 atm. The retention time of the samples in the atmosphere of hydrogen was varied to obtain the different hydrogen concentrations. The hydrogen concentrations were determined by the volume (during hydrogenation) and gravimetric method. When the H-concentration in the sample reaches a certain value, the system automatically removes hydrogen from the samples, and then slowly (1.5 °C/min) decreases the temperature of the sample up to the room temperature in vacuum. The hydrogen concentration values obtained in this experiment were in the range of 0.9-25.1 atm %. This means that, in accordance with the Ti-H diagram, the new phases can be formed during hydrogenation.

3. Results and discussion

Methods. Spectra of PL in the samples were collected using the spectrometer described in details in [6]. The time resolution of this spectrometer is 240 ps. Three spectra of $5 \cdot 10^6$ events each were collected for every sample. They were mathematically fitted by the sum of 1 gaussian and several exponential functions according to the two-state trapping model by the LT10 software [18]. After the background and the source contribution subtracting, decomposition of the spectra was carried out by two exponential components. Each component is characterized by the positron lifetime (τ) and intensity (I) values [19-21]. Figures 1-2 show the results of measurements for the intensity I and the positron lifetime (τ) versus the hydrogen concentration in titanium.

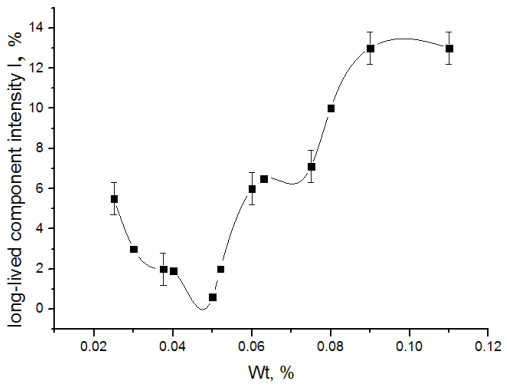

Figure 1. Intensity of EPA versus the concentration of hydrogen in titanium.

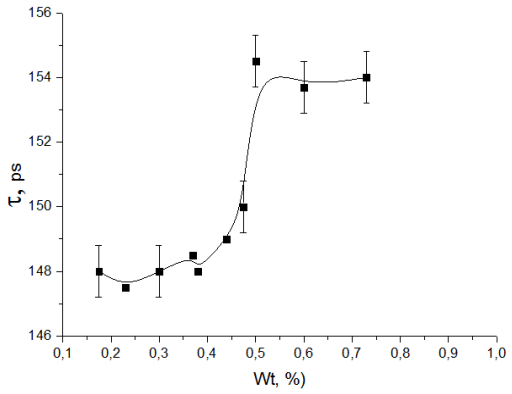

Figure 2. Positron lifetime in titanium versus the concentration of hydrogen in the BT1-0 titanium samples.

After the formation of defects, the curve *I* (wt) reaches the plateau region when the concentrations of hydrogen in titanium are in the range of 0-5 wt%. The increase in the concentration is also characterized by the increase in the lifetime of positrons (Figure 2). It should be noted that there is the inflection point on the curve of the thermal electromotive force for the same concentration (Figure 3).

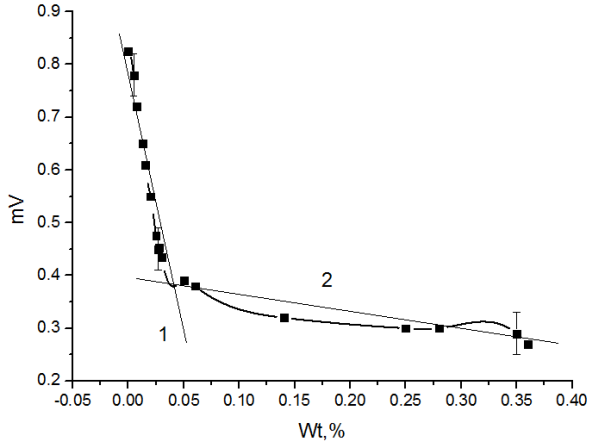

Figure 3. Thermal electromotive force versus the concentration of hydrogen in titanium BT1-0.

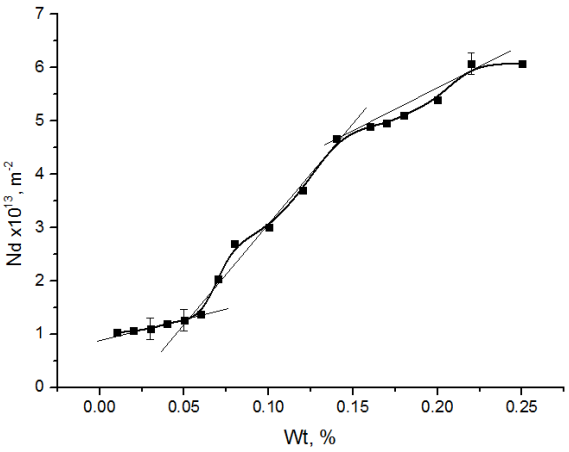

Figure 4. Number of defects versus the weight content of hydrogen (w_t) in the titanium alloy.

The relative change in the absolute coefficient of the thermal electromotive force S is determined by the formula [23] (1, 2):

$$\frac{\Delta S}{S_0} = \frac{3\pi^2 \hbar Q}{e^2 k_F^2 \rho}\left(\frac{\Delta x}{x} - 1\right) \tag{1}$$

$$x = -\frac{k_F}{2}\left(\frac{d \ln}{dk}\rho_0\right)_{k=k_F}$$

$$\Delta x = -\frac{k_F}{2Q}\left(\frac{dQ}{dk}\right)_{k=k_F} - 1. \tag{2}$$

In the formulas (1-2), *Q* is the transport cross-section of electron scattering in a defect, *Kp* is the wave vector on the Fermi surface, *p* is the specific resistance of the metal, *e* is the electron charge, *h* is the Planck's constant. This value depends on the value of the transport cross-section of electron scattering *Q* in the defect, the specific resistance of hydrogenated titanium, i.e., on the number of defects and the shape of the cross-section.

It follows from the formula (1) that the value *ΔS/S* is determined by the value *Δx/x*, the cross section of scattering *Q*, and a possible change in the sign of the derivative *dQ*/*dk* caused by the presence of defects. Figure 3 shows the inflection point for the thermal electromotive force versus the concentration of hydrogen in titanium, which is caused by the transition of titanium from one structural state to another one.

A further increase in the hydrogen concentration does not lead to the changes in the thermal electromotive force and is completely dependent on the transport cross-section of electron scattering in the defect, i.e., on the number of defects and the shape of the cross-section and is indirectly confirmed by the measurements shown in Figure 4. This fact is typical when there are the changes in the structure of the titanium alloy. The further increase in the hydrogen concentration does not lead to the changes in the thermal electromotive force. The jump in the change of the thermal electromotive force can be

explained by the formation of a chemical compound (hydrogen with titanium), the presence of the phase transition $\alpha \rightarrow \gamma$ and grains, as well as the different material in intergranular zones. If to draw a tangent to the curves and drop a perpendicular to the axis of concentrations, then the obtained value of the hydrogen concentration in the metal corresponds to the concentration of titanium during the transition in the different structural state.

The number of defects in titanium N_d versus the hydrogen concentration is shown in Figure 4. In this work, the dislocation density of N_d is determined by formula (3) using the method described in [22]:

$$N_d = \pi\beta^2 ctg^2\Theta / 16b^2, \quad (3)$$

where β is the broadening of X-ray lines caused by microdeformation of the lattice, Θ is the angle corresponding to the peak of the X-ray line, *b* is the Burgers vector.

There are three regions (0.01-0.05) wt%, (0.5-0.14) wt% and 0.14- 0.24 wt%. The results for these regions are similar to the results received by the EPA method (Figure 1 and 2). If to draw a tangent to each region and drop a perpendicular from the point of intersection, then we obtain the concentration of hydrogen in titanium, the value of which corresponds to the change in the hydrogenation of the sample. A comparison of Figures 1-4 shows an identical character of the dependences with a characteristic inflection point on the curve of the hydrogen concentration that is equal to 0.05 wt% for the thermal electromotive force and a good agreement between the EPA (Figure 2) and N_d (Figure 4) values. This effect can be used to estimate the transition of the titanium alloy from one state to another one in order to control the material and allows this technique to be introduced for the laboratory and industrial control.

4. Conclusion

This method proposed for controlling the changes in the structure of titanium saturated with hydrogen is based on the simultaneous use of electron-positron annihilation and the measurement of the thermal electromotive force and electrical resistance. The results have shown that there are two characteristic regions in which hydrogen in titanium has an effect on the value of the thermal electromotive force. The characteristic graphic inflection found for the thermal electromotive force versus the hydrogen concentration allows us to determine the concentration of hydrogen in titanium, the value of which corresponds to the structure rearrangement of the titanium alloy. The transition from one structure to another one is shown to be observed for the value of the hydrogen concentrations in titanium equal to about 0.5 wt%. A comparison of the structural-phase state for the titanium alloy such as TiH_2: 4.04 wt% TiH: 2.02 wt% $TiH_{0.5}$: 1.01 wt% allows us to control the compounds of titanium with hydrogen using the measurements of the thermal electromotive force obtained for the thermal electromotive force versus the concentration of hydrogen in titanium.

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