

# Measurements of Hydrogenated Titanium by Electric Methods

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**Abstract.** The titanium alloy (VT1-0) was investigated during the hydrogenation in gaseous atmosphere at the temperatures of 600 °C using the Sieverts method. The samples were analyzed with the eddy and direct currents. The dislocation density ( $N_d$ ) was calculated as a function of the weight concentration of hydrogen in titanium according to X-ray spectra. The X-ray line broadening method was used. The value  $N_d$  was associated with the electrical resistivity  $\rho_d$  of hydrogenated titanium. The phase composition was analyzed using the database (PCPDFWIN and PDF-4+) and the full-profile analysis programs (POWDER CELL 2.5). The change in the hydrogenation of titanium leads to a change in the concentration of defects and the behavior of eddy currents depending on the frequency. This indicates a change in the hydrogen concentration through the thickness of the sample. The concentration of hydrogen was changed in depth using a spectrum magnetic analyzer (SMA II, Germany). The direct current resistivity of the titanium samples was measured by the four-probe method using a software complex «KEIHLEY INSTRUMENTS». The relationship was found between the hydrogenation degree and the electrical conductivity of a titanium alloy, which allows us to quantitatively measure the number of defects generated by hydrogen in titanium, using the eddy and direct currents. These results can be used in specific applications for the combined electrocurrent analysis of hydrogen in metals.

## INTRODUCTION

The best known ways to control the presence of hydrogen and other gases in metals are the microhardness measurement methods, as well as the X-ray and photometric analysis. These methods are used under laboratory conditions. These methods are inefficient in the high-volume manufacturing control and the detection of local gas-saturated areas. This work is devoted to the development of the method for studying the hydrogenation of titanium by electric currents. To compare the results, the X-ray analysis is applied. The electrical resistivity of metals is known to be changed during the gas saturation [1]. Hydrogen occupies a special place among all kinds of gas interstitial impurities. Hydrogen is redistributed and accumulated in the volume of material, which can lead to the release of hydrides and the formation of pores and cracks. The use of eddy currents is reasonable due to the fact that the defects of metals are located at different depths. The electrical resistivity  $\rho_d$  was calculated versus the density of defects  $N_d$  using the model that includes the dilatation of the lattice and the existence of the quasi-stationary resonance electron states near the Fermi energy. This model explains quantitatively the contribution of dislocations and other defects to the electrical resistivity of metals. The aim of this paper is to investigate propagation regularities of electric currents in hydrogenated titanium alloy VT1-0.

## METHODS AND MATERIALS

Titanium VT1-0 was studied in the following composition [% wt.]: 0.18 Fe; 0.1 Si; 0.07 C; 0.12 O; 0.01 H; 0.04 N. The content of the elements corresponds to the passport data of commercially pure titanium. The hydrogenation was carried out by the Sieverts method. The hydrogen concentration was measured by the hydrogen

analyzer RHEN602 (LECO). The dislocation density in titanium was determined according to the X-ray line broadening by using the diffractometer Shimadzu XRD-6000 for the Cu-K $\alpha$  radiation. The phase composition was analyzed using the databases (PCPDFWIN and PDF-4+) and the full-profile analysis program (POWDERCELL 2.5). The concentration of hydrogen was changed in depth using a spectrum magnetic analyzer (SMA II, Germany) [2, 3]. The direct current resistivity of the titanium samples was measured by the four-probe method. To study the structure of the alloy surface, the methods of optical (OLYMPUS) and scanning (microscope Philips SEM 515) microscopy were used.

The changes in the electrical resistivity  $\rho_d$  per unit density of defects  $N_d$  versus the concentration of hydrogen in metal were estimated by the formula [6]:

$$\rho_d / N_d = \hbar k_F \Omega_a Q / n_s e^2 \quad (1)$$

where  $k_F$  is the value of the wave vector at the Fermi level,  $\Omega_a$  is the atomic volume,  $Q$  is the transport cross section for the scattering of electrons,  $n_s$  is the number of the current carriers per atom,  $e$  is the value of the electron charge. The transport cross section of scattering  $Q$  is the superposition of the resonance  $QR$ , potential  $QP$  and interference  $QI$  components [7]:

$$Q = QP + QR + QI \quad (2)$$

The value of the individual components depends on many factors. In particular, the grain structure of titanium and other metals with a high level of hydrogenation determines mainly the value of the electrical resistivity and depends on the state of the hydrogen subsystem in the hydrogenated metal. The curve in Fig. 4 can be explained by the change in the contribution of various components to the transport cross section of scattering depending on the concentration of hydrogen in titanium. The structure of the titanium alloys is heterogeneous: there are the grains with a size of 10 ... 15 microns along with the grain size of 50 ... 100 microns. In this case, the dislocation density reaches  $10^9 \text{ m}^{-2}$ . For nonequilibrium nano- and GMC materials, the dislocation density is  $\sim 2 \cdot 10^{14} \text{ m}^{-2}$  [9]. In particular, it relates to titanium. This should be considered in the study of the energy storage in materials through the creation of the boundaries with the specific properties. The works [8, 9] provide the information on the change in the grain boundary structure, which leads to a change in the proportion of resonance electron scattering by the linear defects that form the boundary.

The electrical resistivity per unit density of dislocations for the evident grain structure, in this case, can be estimated by the formula

$$\frac{\Delta\rho_d}{N_d} = \frac{3\pi^2 \hbar Q}{e^2 k_F^2} \quad (3)$$

where  $N_d$  is the density of dislocation. This value is approximately equal to  $N_d = (106-107) \text{ cm}^{-2}$ ;  $\Delta\rho_d/N_d = (1-2) \cdot 10^{-19} \text{ Ohm} \cdot \text{cm}^3$  [9]. The high experimental value of the electrical resistivity for dislocations [10] is usually explained by the resonance scattering of electrons in the dislocation center. If to consider only the resonance scattering of electron waves [11], when all the dislocations are perpendicular to the flow of electrons, it leads to the maximum value of the resonance cross-section for scattering  $QR$ . This value is less than that for the random distribution of dislocations and depends on the incidence angle of an electron wave on the grain boundary and can be greatly changed versus the value of the incidence angle.

Therefore, there is no need to consider the interference effects, the contribution of which to the electrical resistivity is much smaller than the contribution of the dislocation centers. This is due to the fact that the electrostatic interaction in metal is screened by the conduction electrons at the interatomic distance. Elastic fields in the dislocation also have a little effect on the increase in the resistivity. However, this statement requires additional studies for titanium.

The effective wave vector of the conduction electrons is calculated by the formula [12]:

$$k_F^* = (3\pi^2 n_e)^{1/3}, \quad (4)$$

where  $n_e = n_s / \Omega$  is the concentration of effective charge carriers per unit volume;  $\Omega$  is the atomic volume. The values  $94-370) \cdot 10^{13} \text{ microohm} \cdot \text{cm}^3$  were previously received for pure titanium  $\rho_d/N_d$ . At the same time, the experimental value was  $1 \cdot 10^{15} \text{ microohm} \cdot \text{cm}^3$  for titanium and zirconium.

In this study, the specific resistivity was measured by the four-probe method for each concentration  $w_t$  of hydrogen in titanium. The dislocation density  $N_d$  was determined by the method described in [13, 14]:

$$N_d = \pi\beta^2 \text{ctg}^2 \Theta / 16b^2, \quad (5)$$

where  $\beta$  is the broadening of X-ray lines caused by the lattice microdeformation,  $\theta$  is the angle corresponding to the maximum of X-ray lines,  $b$  is the Burgers vector.

The samples were prepared from the VT-1-0 alloy with the different thicknesses from 1 mm to 10 mm and then saturated with hydrogen in the gas phase at the temperature of 600 °C and the pressure of 2 atm. After the saturation with hydrogen, the samples were measured by the eddy and direct currents and the X-ray diffraction method. Then the samples were melted using the LECO-600 device to determine the amount of hydrogen.

## RESULTS AND DISCUSSION

The greatest amount of hydrogen sorbed by titanium was observed for the sample with a thickness up to 3 mm (Fig. 1). Figure 1 shows a relatively uniform hydrogen absorption by the samples with a thickness more than 3mm. The further increase in the thickness (for the same surface area, time and temperature of hydrogenation) is not accompanied by the change in the concentration of hydrogen in titanium. The increase in the hydrogen concentration leads to the change in the metal structure, the formation of defects, which is illustrated in the Fig. 2. The method for calculating the density of dislocations will be described below.

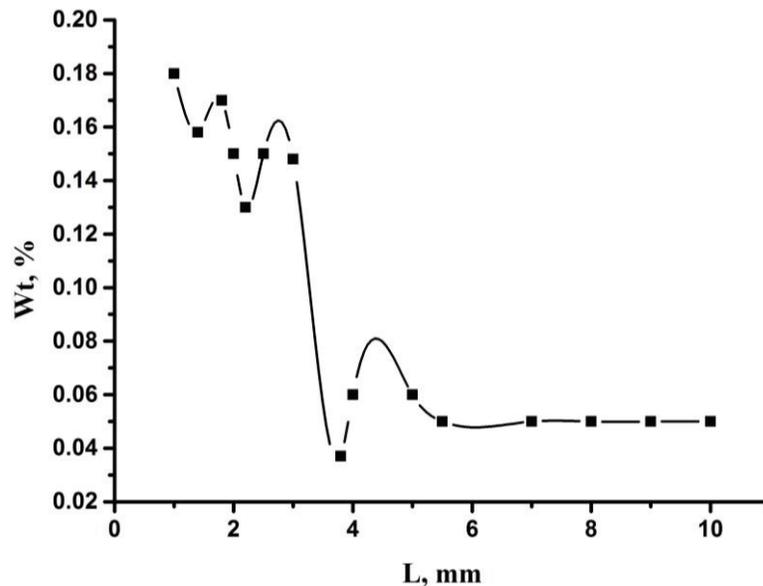


FIGURE 1. Concentration of hydrogen in titanium (wt.%) versus the thickness of the sample

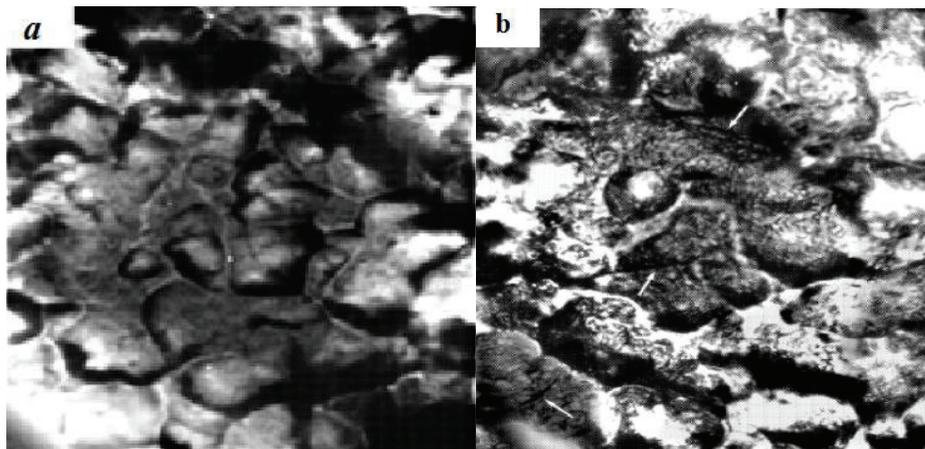


FIGURE 2. Initial surface of titanium VT1-0 (a) and after hydrogenation (b). Metallography. x 1000

Hydrogen interacts with the existing structural defects and initiates the formation of new defects and dislocations [1, 2]. This leads to the changes in the electrical resistivity. The presence of hydrogen is accompanied by the broadening of the grain boundaries. The grains became "loose" [4, 5]. This conclusion follows from the analysis for the surface of initial and hydrogenated titanium (Fig. 3).

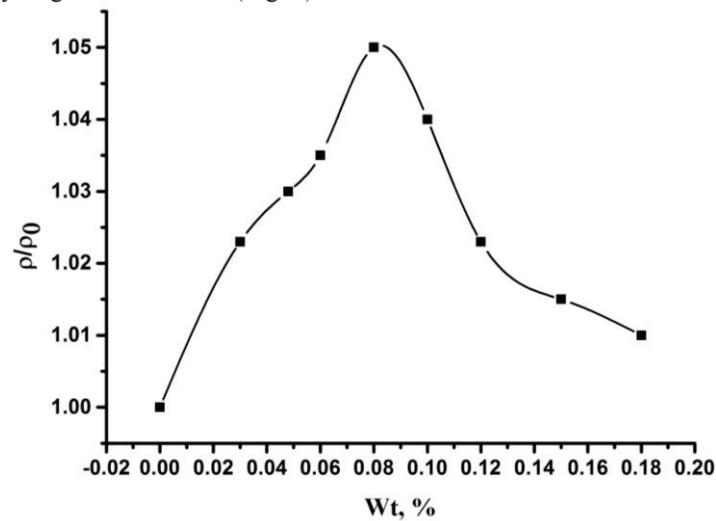


FIGURE 3. Relative resistivity of hydrogenated titanium versus the hydrogen concentration in titanium (b)

The grain structure of the titanium alloy surface is well seen using the methods of optical (OLYMPUS) and scanning (Philips SEM 515 microscope) microscopy Fig. 2. The size of grains is changed (indicated by arrows). It is likely to lead to a change in the cross section for the scattering of electron waves on the grains and boundaries and to the change in the electrical resistivity for both the direct current and the high-frequency eddy current. Fig. 3 shows the relative change in the electrical resistivity versus the concentration of hydrogen in titanium. The curve has a characteristic maximum. This can be explained by the fact that the grain boundary dislocations are located at the different distances up to a dozen of interatomic distances. We should emphasize that the diagram in Fig. 3 is similar to the results received for palladium [1].

The studies concerning the structural and phase state of the titanium alloy (Table 1) in the initial and hydrogenated state showed the presence of the  $\alpha$ -phase in Ti with a hexagonal lattice at all the reflection angles of X-rays. After hydrogenation, the values of the parameters are equal to  $a = 2.9461 \text{ \AA}$ ,  $a = 2.9430 \text{ \AA}$ , and  $c = 4.6818 \text{ \AA}$  and are changed with increasing the hydrogen concentration. The X-ray diffraction analysis of the samples showed the presence of the  $\text{TiH}_{1.5}$  phases in the layers in the amount of 7.4%, and also  $\text{Ti}_6\text{O} - 36.8\%$ ,  $\text{TiO}_2 - 6.1\%$ . At the same time, the percentage of impurities significantly depends on the amount of hydrogen added. It should be noted the change in the size of crystallites that can lead to a change of  $\rho_d$  (Table 1).

TABLE 1. The X-ray study of titanium VT1-0 (part of the table is shown)

Concentration H, wt. %	Detected phases	Concentration of phases, wt. %	Parameters of lattice, 0.1 nm	Size of crystallites, nm
0.04	Ti_hexagonal	93.31	$a = 2.9461$ $c = 4.6818$	71
	TiH <sub>1.5</sub> _cubic	0.59	$a = 4.4064$	195
	TiO <sub>2</sub> _tetragonal	6.09	$a = 4.5849$ $c = 2.9703$	28
	Ti_hexagonal	53.53	$a = 2.9430$ $c = 4.6746$	>300
0.07	TiH <sub>1.5</sub> _cubic	7.42	$a = 4.4079$	>300
	TiO_cubic	2.28	$a = 4.2729$	>300
	Ti_hexagonal			

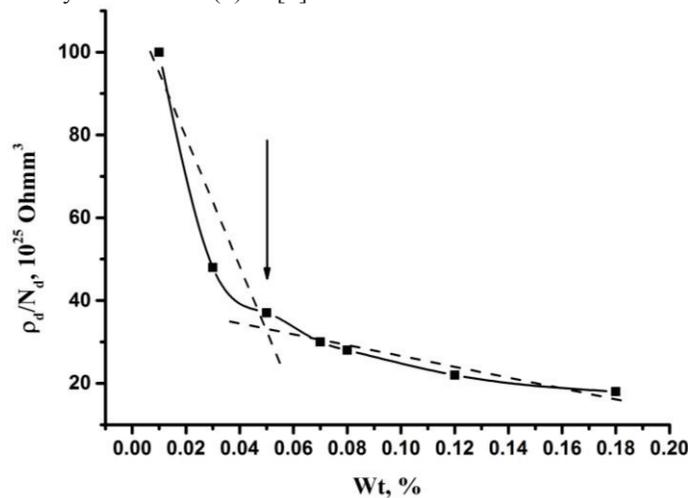
The atomic volume was estimated by the formula  $\Omega_a = a_0^3 / 4$ . The number of current carriers per atom  $n_s$  was selected by the method described in [7]. This method was used in [9] to estimate the effective concentration of carriers in the transition metals (Ni, Ti, Zr, Co), for the case when the density of the states at the Fermi level in the  $d$ -zone was significantly higher than the corresponding parameters  $s$  in the  $d$ -zone, since the population  $M_d \gg M_s$ . In this case, the concentration of carriers is determined from the average atomic magnetic moment per atom  $\mu$ . Thus, the concentration of carriers in the  $s$ -zone is equal to  $n_s = 0.54$  e/atom for nickel at  $\mu = 0.54 \mu_B$  and 10 ( $s + d$ ) electron per atom. In cobalt with 9 ( $s + d$ ) electrons, the values are equal to  $\mu = 1.72 \mu_B$  and  $n_s = 0.72$  e/atom. For transition metals (Ti, Zr, Mo and others) with vacant states in the both subzones, the scattering of electrons in the free states of the  $s$  and  $d$  zones is proportional to the state density of these zones at the Fermi energy [7, 15]. The calculations of  $n_s$  for Ti, Zr, Mo, and W are given in [11]. For Ti ( $n_s$ ) = 0.065, Zr ( $n_s$ ) = 0.065, Ni ( $n_s$ ) = 0.54, and W ( $n_s$ ) = 0.24, Mo. Thus, the semi-empirical calculation of the transport cross section for the scattering of electrons by the formulas (1-4), taking into account the  $n_s$  values for titanium and various concentrations of hydrogen, results in the following values  $Q$ .  $Q$  ( $w_H=0.05$ )  $\approx 2A^0$ .  $Q$  ( $w_H=0.18\%$ )  $\approx 8A^0$ . The characteristic maximum is observed for ( $w_H=0.078\%$ ).

**TABLE 2.** The width of X-ray reflections at half maximum versus the concentration of hydrogen in titanium (part of the table is shown)

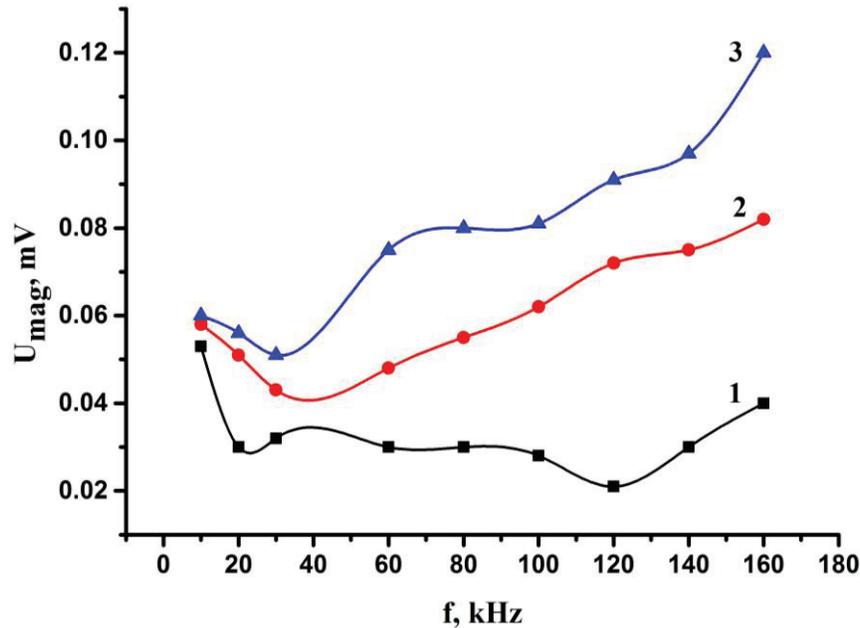
Concentration of hydrogen content in titanium, wt%	0.03	0.05	0.08	0.12	0.16
Width of the X-ray peak at half maximum in the direction 100	0.135	0.200	0.276	0.350	0.390

The change in the width of the X-ray (Table 2) reflections allows us to determine the value of the parameter  $\beta$  that is included in the formula (5). There are the two linear dependences for the density of dislocations versus the weight concentration of hydrogen in the titanium alloy (Fig. 4). The change of the  $\rho_d/N_d$  parameter versus the hydrogen concentration in titanium is recessive, which can be explained by the decrease in the total transport cross section of scattering  $Q$  (Eq. (1)). When the weight concentration reaches about  $w_H = 0.12\%$ , this parameter becomes constant, i.e. the decrease in the transport cross section of scattering  $Q$  is compensated by the increase in the atomic volume  $\Omega_a$ . The value of the atomic volume was calculated according the data in Table.

In addition, the contribution of different scattering components can be changed (formula (2)). This is connected with the change in the amount of titanium hydrides and the nature of dislocations, as well as with the formation of vacancies. The experimental data (Fig. 1) are in good agreement with the theoretical values  $(94.3 - 370.4) \cdot 10^{-25}$  Ohm  $m^3$  calculated for titanium by the formula (1) in [3].



**FIGURE 4.** Electrical resistivity  $\rho_d$  per unit density of defects  $N_d$  versus the concentration of hydrogen in metal



**FIGURE 5.** Eddy current sensor readings versus the eddy current frequency (1- is the initial sample, 2 is titanium saturated with hydrogen ( $w_t = 0.02\%$ ), 3 - ( $w_t = 0.07\%$ ) (b)

In Fig. 4 the arrow shows the inflection point for the ratio  $\rho_d/N_d$  versus the concentration of hydrogen in the titanium alloy. This point was obtained by drawing the tangents to the two curves. Such point corresponds to a phase transition of titanium observed at a concentration ( $w_t = 0.05\%$ ). This phase transition is observed for the titanium alloy VT1-0. For this concentration of hydrogen in the titanium alloy, the  $\delta$  - hydride was found using the alternative lengthy methods for measuring the positron annihilation [16]. The inflection of a curve is caused by two reasons: 1) hydrogen is accumulated mainly in the surface layers; 2) the layer consisting of  $\delta$  - hydrides of titanium is formed in the surface layers of titanium during hydrogenation, as stated in [2]. Hydrogenation of titanium is accompanied by the change in the readings of the magnetic spectrometer versus the frequency of the eddy current (Fig. 5, part of the graph is shown). The initial and hydrogenated samples have the smallest difference at low frequencies, when the eddy current penetrates into the sample as much as possible. The results in Fig. 6 allow us to form nomographs for the nondestructive control and determination of the hydrogen concentration in the titanium alloy. Each frequency of the eddy current corresponds to a certain depth of penetration into the titanium alloy.

## SUMMARY

Thus, the simultaneous measurement and comparison of eddy currents with the measurements of direct currents can serve as an additional tool for the analysis of physical processes during the hydrogenation of titanium and be useful in practical purposes. The received results indicate that the combined approach provides an effective way of controlling the concentration of hydrogen in the titanium alloy and can be used for other materials. The ratio  $\rho_d/N_d$  versus  $w_t$  allows us to determine the concentration of hydrogen in titanium resulting in the formation of the  $\delta$  - hydrides of titanium. The mechanical characteristics of the material can be determined at this point.

## ACKNOWLEDGMENTS

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