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Thermo-Electromotive Force and Electrical Resistivity of Hydrogenated VT1-0 Titanium Alloy

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Abstract. The method for measuring the structure transition of hydrogenated titanium from one state to another is suggested. The method is based on the comparison of thermo-electromotive force (thermo-emf), DC electrical resistance and the results of X-ray diffraction analysis. X-ray diffraction analysis is applied for identifying the quantity of defects in titanium structure. The authors have also identified the identical dependence of thermo-electromotive force and electrical resistivity on hydrogen concentration in titanium. The effect can be used for hydrogenated titanium structure control.

1. Introduction

Complex structural changes occur in titanium products during their operation. They suffer the formation of gas-saturated layers containing interstitial phases of oxygen, nitrogen and hydrogen with different concentration along depth. This complicates mechanical treatment, reduces metal plasticity, and reduces the performance of the components [1-3]. Gases are controlled and outgassed using different methods; protective media and coatings or vacuum heating are used [3, 4]. Due to this, sections which differ from one another are formed on titanium surface. These local structural defects lead to the destruction of components during their operation. If a submicrocrystalline structure is formed in titanium, this leads to the increase of capacity to accumulate hydrogen in titanium [5, 6]. It is caused by the increase of grain boundary length in submicrocrystalline samples in comparison to coarse-crystalline ones. The most well-known methods to control the presence of hydrogen and other gases in metals are the methods of microhardness measurement, X-ray diffraction and photometrical analysis [1, 2, 6, 7]. These are laboratory methods, and they are difficult to use for mass manufacturing inspection and are ineffective for detection of gas-saturated parts.

The present work focuses on the development of a technique for detecting defects in the microstructure of hydrogenated titanium by measuring thermo-emf and electrical resistivity using X-ray diffraction analysis.

2. Materials and Methods. Experimental Procedure

Annealed samples of commercially pure titanium (Fe-0.18; Si-0.l;C-0.07; N-0.04; O-0.12; H-0.01) with the dimensions of 10.0x5.0x1.0 mm and 100.0x28.0x1.0 mm were chosen for the experiment.

Hydrogen saturation was performed using Gas Reaction Controller according to Sieverts' method at the temperature of 300 – 600 °C, pressure of 0.6 and 2 atm. and time of hydrogenation of up to 300 minutes [4]. As a result of the treatment, the samples with the mass content of hydrogen of 0.0008 – 0.4 wt% were obtained. Hydrogen concentration in VT1-0 samples was determined using RHEN 602 (LECO) gas analyzer. Dislocation density in titanium was determined by broadening of X-ray lines using Shimadzu XRD-6000 diffractometer with Cu-K_α source. The analysis of phase composition was performed using PCPDFWIN and PDF-4+ databases and POWDER CELL 2.5 depth profile analysis software.

The measurement of titanium sample DC resistivity was performed by 4-probe method [7] using KEIHLEY INSTRUMENTS instrument control software. EMF was measured using T-3SP setup with increased pressing of electrodes to the sample.

3. Results

The following equation 1 was used to estimate the change in dislocation electrical resistivity taken relative to the unit of their density N_d in the unit of volume depending on hydrogen concentration in titanium [8]:

$$D = \frac{\rho_d}{N_d} = \frac{\hbar k_F \Omega_a Q}{n_s e^2}, . \tag{1}$$

where k_F is the value of propagation vector on Fermi level, Ω_a is atomic volume, Q is electron transport cross section, n_s is the number of charge carriers per atom, e is the charge of electron, n_s is the number of charge carriers.

Density of dislocations N_d was determined using the Equation 2 from [9] based on X-ray diffraction analysis of titanium samples:

$$N_d = \pi\beta^2 ctg^2\Theta / 16b^2, . \tag{2}$$

where β is the broadening of X-ray lines caused by lattice microdeformation, θ is the angle that corresponds to the X-ray line peak, b is the Burgers vector. The resistivity of the samples was measured by probe method for each hydrogen weight concentration in titanium [10]. The increment of the resistivity connected with the unit of density of chaotically distributed dislocations $\Delta\rho_d / N_d$ was calculated as

$$\Delta\rho_d / N_d = \frac{3\pi^2 \hbar Q}{e^2 k_F^2}. \tag{3}$$

where N_d is dislocation density that was determined from X-ray measurements [9]. The increment of emf absolute coefficient equals to [11-13]

$$\Delta S = S_0 \frac{\Delta\rho_d}{\rho}\left(\frac{\Delta x}{x} - 1\right), . \tag{4}$$

where

$$\rho = \rho_0 + \Delta\rho_d ; \rightarrow x = -\frac{k_F}{2}\left(\frac{d\ln}{dk}\rho_0\right)_{k=k_F} ; \rightarrow \Delta x = -\frac{k_F}{2}\left(\frac{d\ln\Delta\rho_d}{dk}\right)_{k=k_F} = -\frac{k_F}{2Q}\left(\frac{dQ}{dk}\right)_{k=k_F} - 1.$$

Thus, the thermo-emf fraction change S is calculated as

$$\frac{\Delta S}{S_0} = \frac{3\pi^2 \hbar Q}{e^2 k_F^2 \rho}\left(\frac{\Delta x}{x} - 1\right). \tag{5}$$

and is totally dependent on the value of cross-section of electron scattering after interacting with defects, i.e. on the quantity and cross section shape of the latter. Such phenomenon is typical for the change of titanium alloy structure. According to Equation 5, the ratio $\Delta S/S$ is falling with the steepness depending on the value of Δx and scattering cross-section Q with distinctive inflection. In Figure 1, there is the inflection of emf dependence on hydrogen concentration in titanium, which is caused by titanium transition from one structural state to another. Further increase in hydrogen concentration does not change emf. Jump of emf can be explained by the formation of a chemical compound of hydrogen and titanium. Phase transition $\alpha \rightarrow \gamma$ is observed within the given hydrogen concentrations. With tangents drawn (as shown by numbers 1 and 2) to the given areas of diagram and a perpendicular dropped to the axis of distribution, the obtained value of hydrogen concentration in metal conforms to the concentration of titanium transition to another structural state.

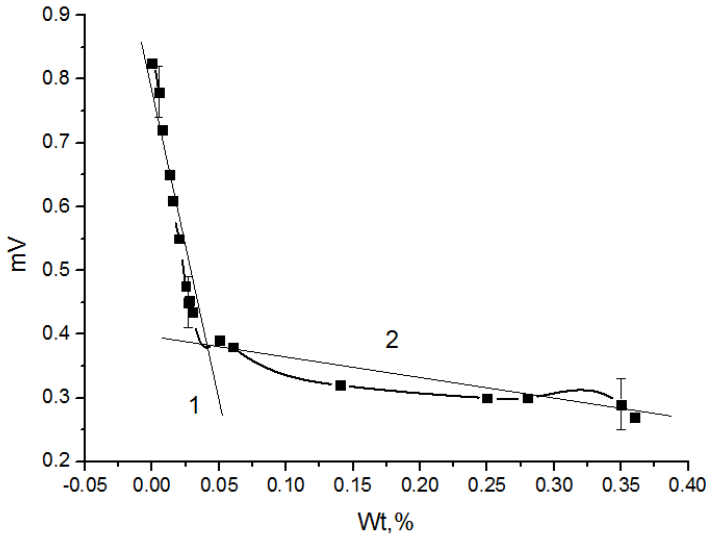

Figure 1. Dependence of thermo-emf on hydrogen concentration in titanium VT1-0.

The dependence of the number of defects in titanium on hydrogen concentration (Eq. 2) is presented in Figure 2.

There are two branches. With tangents drawn to each of the branches and a perpendicular dropped from the intersection of curves we obtain the hydrogen concentration in titanium corresponding to the change of electrical resistivity of the sample. Correlation of diagrams presented in Figures 1-2 gives the identical character of dependencies with a characteristic inflection point at hydrogen concentration of 0.05 wt%. The effect observed during the experiment can be used for evaluating titanium alloy transition from one state to another for controlling the state of the material. Accounting the pressing of electrodes to the tested sample allows implementing this method for laboratory and industrial control.

4. Conclusion

The suggested method for controlling the hydrogenated titanium structure is based on the simultaneous measurement of thermo-emf and electric resistivity. We have established two typical regions corresponding to the influence of hydrogen presence in titanium on the value of thermo-emf. The discovered indicative inflection of the dependence of thermo-emf on hydrogen concentration enables the determination of hydrogen concentration in titanium that coincides with the initiation of titanium alloy restructuring. We have shown that the transition from one structure to another is obvious even at hydrogen concentration in titanium of about 0.5 wt%. The correlation of structure and phase composition of titanium alloy as Ti H_2 : 4.04 wt% Ti H : 2.02 wt% Ti $H_{0.5}$: 1.01 wt% allows

controlling the types of titanium-hydrogen compounds by measuring thermo-emf and using the plot thermo-emf vs. hydrogen concentration in titanium.

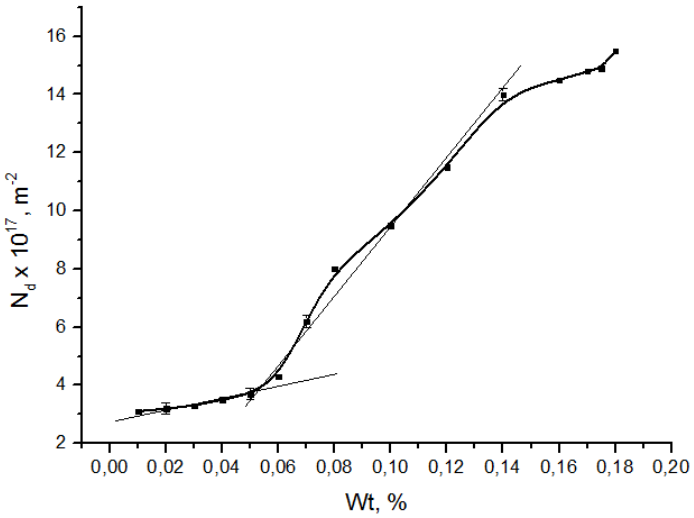

Figure 2. Dependence of number of defects on weight hydrogen content w_t in titanium alloy.

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