

Measuring the dislocation density of VT1-0 titanium alloys with different content of hydrogen by x-ray diffraction method

S P Xu^{1,2}, V N Kudiiarov¹, K Li¹ and V V Larionov¹

¹Division for Experimental Physics, School of Nuclear Science & Engineering, National Research Tomsk Polytechnic University, Lenin Avenue 30, Tomsk, 634050, Russia

E-mail: isxusp@gmail.com

Abstract. In this study, the distributions of dislocation density with hydrogen concentration in titanium VT1-0 were obtained. The samples with different hydrogen concentrations was carried out by using the Sieverts method. The dislocation densities were obtained by using the full width at height medium calculations from the XRD results of Gaussian approximation fitting. For accurate calculation of the dislocation density in titanium alloys, the double-line separation phenomenon of the XRD results and the variation of the Burgers vector in different lattice directions were considered. The phenomenon of the double-line separation is more evident when the diffraction angle 2θ is larger than 40° . The mean value of dislocation density for the different hydrogen concentrations is about $10^{13} \sim 10^{14} \text{ m}^{-2}$. Moreover, as the increases of hydrogen content in the titanium alloy, the dislocation density also increases.

1. Introduction

Due to their high strength, modulus of elasticity and toughness, titanium and titanium alloys are used in a wide variety of aerospace, energy, and biomedical [1]. Recent advances in titanium alloy lead to understanding that studies of hydrogen-titanium system are important. Moreover, titanium alloys are considered for a variety of applications. In many cases, hydrogen changes the plasticity of most metals and alloys [3]. These properties are highly dependent on material texture, dislocation density, dislocation sliding, etc. Therefore, in order to predict the characteristics of materials and design materials with certain properties, the understanding of the deformation process from the microstructure parameters is crucial. The most well-known methods for measuring the presence of hydrogen and other gases in metals are the methods for measuring micro-hardness, x-ray diffraction (XRD), and photometric analysis [4]. These methods are laboratory methods, their use is difficult for production control and is ineffective for detecting local gas-saturated areas. Plastic deformation is the direct cause of dislocation motion, used the methods of statistical mechanics consistently with three-dimensional systems of curved dislocation lines also developed the mathematical foundations for calculating of the dislocation density [5]. In recent years, the XRD method has been used to calculate the dislocation density in materials [6], and in the method, the Burger vector influences the calculation. There are some studies on the Burger vector of materials different types [7]. The structure of titanium alloys is heterogeneous; the grain of the titanium is $10\text{--}15 \mu\text{m}$ or $50\text{--}100 \mu\text{m}$ in size. In this case, the dislocation density reaches 10^9 m^{-2} . In particular, this refers to the study of the accumulation of energy in materials by creating boundaries. Information on the change in the structure



of the grain boundaries leads to a change in the fraction of the resonance scattering of electrons on linear defects forming the boundary [8]. In the previous work, we have already discussed the electrical resistivity ρ_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 [9]. In this paper, we studied the dislocation density in the condition of different radiation for different hydrogen content.

2. Methods and materials

Titanium VT1-0 was studied in the following wt% composition: 0.18 Fe; 0.1 Si; 0.07 C; 0.12 O; 0.01 H; 0.04 N. For this research, we prepared samples with dimensions of $20 \times 20 \times 1$ mm. The samples were cut from a sheet of titanium alloy VT1-0 by the method of electrical discharge machining (EDM). The surface of the specimens was mechanically polished to remove the oxide film. To remove defects and surface stresses, the samples were annealed in vacuum at 750°C for 60 minutes. To obtain different hydrogen concentration in titanium VT1-0, hydrogen permeation in the gaseous medium was carried out at different temperature (about 600°C) and hydrogen pressure in the chamber (about 1-2 atm) on the automated complex Gas Reaction Controller LPB [10]. After saturation, the hydrogen concentration was measured with the hydrogen analyzer RHEN602 (LECOTM). The phase composition and structural parameters of the samples after saturation were determined by an XRD-7000 diffractometer using Cu-K α radiation. The analysis of the phase composition was carried out using the PCPDFWIN and PDF-4 + databases and the full-profile analysis program (POWDER CELL 2.5). The concentration of hydrogen was changed in depth using a spectrum magnetic analyzer (SMA II, Germany) [11],[12]. Used the Philips SEM 515 scanning electron microscope to research the influences of hydrogenation for the surface state of titanium VT1-0; for the survey, the voltage is 20 keV and magnified 500 times.

3. Experimental results and discussion

In recent years, polycrystalline materials with ultrafine structure (grain size respectively less than 1 and $0.1 \mu\text{m}$) and increased length of interfaces, have been intensively developed and investigated [13]. Among the methods for producing ultrafine-grained (UFG) metals and alloys, the most promising are the methods of intense plastic deformation (SPD) from the practical point, which make it possible to obtain the UFG structure in bulk metal blanks. The formation of such a structure using the SPD method leads to an increase in the energy of the interfaces, as a result of interaction with lattice defects. This changes the physical and mechanical properties of metals and alloys. And it is known that grains and phases largely determine the mechanical properties, the nature of the deformation behavior and the destruction of metallic materials.

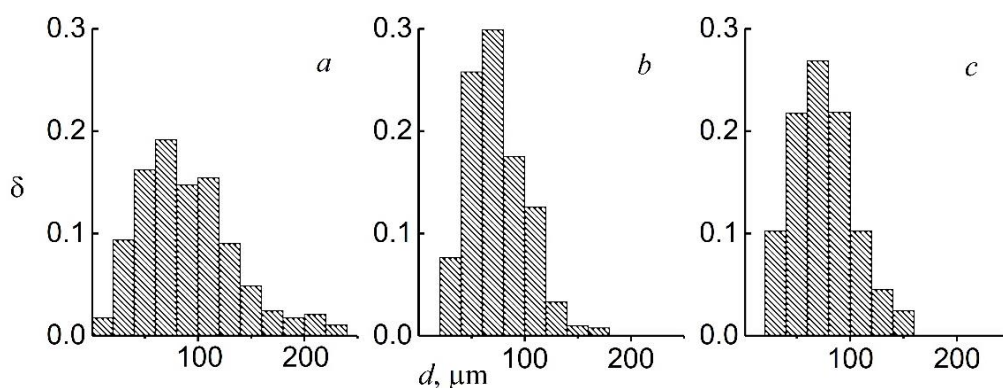


Figure 1. The distributions of grain size *a* – initial alloy VT1-0, *b* – $C_H = 0.052$ mass%, *c* – $C_H = 0.087$ mass%.

By figure 1, we can see the distributions of grain size in titanium VT1-0 with the hydrogen content. It can be clearly seen that after hydrogenation, the larger grain size (50-120 μm) in titanium is significantly increased.

In order to study the dislocation density in materials by XRD, we need to think about the separation of double lines for the $K_{\alpha 1}$ and $K_{\alpha 2}$ x-rays. The separation of double lines is described by the function $\Delta\theta$ (deg) = $\tan\theta \cdot (\Delta\lambda/\lambda) \cdot (180/\pi)$. The Gaussian distribution was applied to the peak. In figure 2 can be observed that the peak splitting occurs, which is associated with strong deformations of the crystal. When the separation was observed at the peak, multiple peaks were attached to the specified curve, and the full width at height medium (FWHM) was determined for each fitting. Furthermore, the averaged values for all these FWHMs were used for the subsequent analysis of the dislocation density.

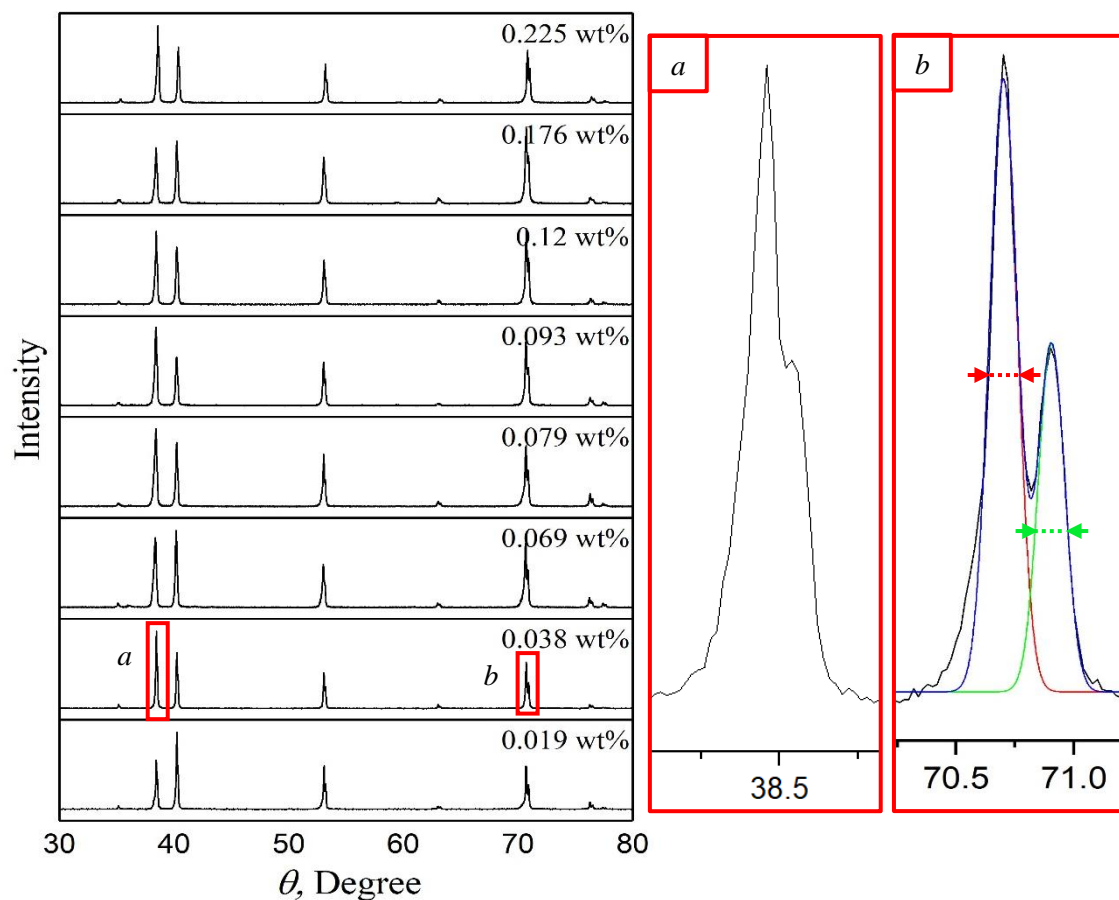


Figure 2. Phase transitions in samples of titanium alloy after saturation with hydrogen. And example of double line separation and full width at height medium for titanium with a hydrogen concentration of 0.038 wt%. *a* – for plane (002), *b* – for plane (103).

Dislocations increase the width of the XRD amplitude (FWHM) curve for three reasons: a) introduces the rotation of the lattice site; b) increases the deformation of the lattice; and c) in the strong damaged crystal, can form a walls-like between small crystals, which leads to a decrease in the size of the crystal. X-ray broadening analysis can be used as a method for calculating the dislocation density. In this work, the calculation of the dislocations density N_d was carried out according to the formula [14]:

$$N_d = \frac{\pi(\beta_{adj}^{(hkl)})^2 \cot^2 \theta^{(hkl)}}{16(b^{(hkl)})^2}, m^{-2} \quad (1)$$

where β is the broadening of X-ray lines caused by the lattice deformation, $\theta^{(hkl)}$ is the diffraction angle corresponding to the maximum of X-ray lines, $b^{(hkl)}$ is the Burgers vector.

By considering the Burger vector from different angles, discussed the result of dislocation density. The Burger vector is obtained in different directions by the model of pure titanium at a normal temperature. At room temperature ($T = 300K$), the titanium alloys have the hexagonal close-packed structure, and the distance between the crystal surfaces can be obtained from the following forms:

$$b^{(hkl)} = d^{(hkl)} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + k^2 + hk) + l^2 \frac{a^2}{c^2}}} \quad (2)$$

Taking into account the phenomenon of diffraction peak separation formed by the $K_{\alpha 1}$ and $K_{\alpha 2}$ x-rays in XRD results (figure 2(b)). Theoretically, the diffraction peak formed by irradiation of x-ray is only related to the atomic arrangement inside the crystal. If the double-line separation phenomenon is not considered, the full width at height medium of the diffraction peak will be larger, especially at a high diffraction angle (cf. figures 2(a) and 2(b)). For the same material, the dislocation density obtained from the diffraction peak formed by x-ray irradiation should be consistent. Therefore, in order to obtain an accurate dislocation density, we have averaged the dislocation density calculated from the diffraction peaks formed by the $K_{\alpha 1}$ and $K_{\alpha 2}$. The result of the dislocation density is shown in figure 3.

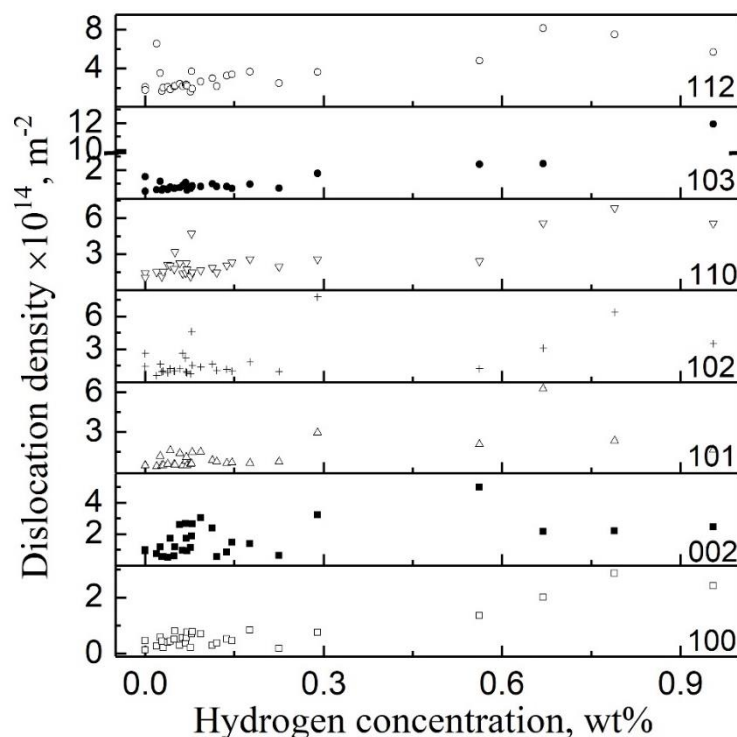


Figure 3. The change in the density of dislocations with hydrogen content for different orientations.

In the process of hydrogen sorption in titanium alloys, hydrides are formed. On the other hand,

hydrogen in the form of atoms or molecules diffuses and migrates into titanium alloys. This will change the phase composition and the lattice structure of the titanium alloys. From the X-ray diffraction results, a change in the internal structure of the material is reflected as a change in the FWHM parameter. Theoretically, we know that grain size decreasing will broaden the diffraction peak. In addition, dislocations and crystal curvature also create conditions for the expansion of the diffraction peak [16]. Thus, under well-known conditions that affect the expansion of the diffraction peak, we obtain the dislocation densities by using equation (1). From the statistical theory, dislocations appear with a greater probability on the plane, where the slip will occur in the crystal. The titanium alloys have the hexagonal close-packed structure, this closest packing structure causes the dislocation lines to randomly appear on any crystal plane. Therefore, the effect on the broadening of the XRD diffraction peak is also random. Considered this random phenomenon, we used the Gaussian fitting when calculating the dislocation density. Therefore, from any crystal plane, we get the statistical results of the dislocation density in the crystal, which should be the same in theory. From figure 3, we can see that, on the planes (110) (102) (101) obtained the roughly consistent results. For the plane (103), due to the formation of the hydride at high concentrations, a peak of hydride formed on the plane, and broadened the diffraction peak. It leads to the anomalously large of the dislocation density. For the plane (112), due to appearing of the diffraction peaks in other orientations (200, 201) at this angle, it also leads to the calculated dislocation density being too large. For the orientations (100) and (002), because the two-line separation phenomenon is not obvious, the results are small by Gaussian fitting. So we chose the average of the dislocation density from the planes (110) (102) and (101). Table 1 shows us the results.

Table 1. The dislocation density for different hydrogen concentration.

Hydrogen concentration, wt%	Dislocation density $\times 10^{14}$, m^{-2}
0.019	0.8537
0.030	1.0048
0.038	1.1783
0.063	1.4940
0.068	1.4795
0.093	1.5127
0.176	1.6855
0.562	1.9001
0.955	3.5647

4. Conclusion

When the X-rays diffraction peaks separation is considered for different orientations, the dislocation density value is approximately $10^{14} m^{-2}$. The distribution of dislocations in the titanium alloy is not related to the lattice orientation. Theoretically, the number of dislocations in the material is not related to the orientation of the diffraction peak. All the factors in the material where the expansion of the diffraction peaks are involved, the dislocation is included. Therefore, whatever diffraction peak is selected, the result of the dislocation density should be similar. From the experimental results, when the diffraction angle exceeds $2\theta=40^\circ$, the results are more consistent. However, for minor diffraction angles do not correspond to the theoretical result, given that the separation of two lines at small angles is not clear, and the approximation of the peaks at small angles, considering the two lines separation, is inaccurate. Consequently, taking into account the two-line separation, a diffraction peak with $2\theta > 40^\circ$ is selected, and the dislocation density can be better approximated. Thus, can be concluded that when the hydrogen content exceeds 0.5 wt%, the dislocation density changes from $(0.1-3)\times 10^{14} m^{-2}$ to $5\times 10^{14} m^{-2}$, due to the formation of hydrides in the material with increasing hydrogen content.

Acknowledgments

This work was granted within the framework of realization of Strategic Programme on National

Research Tomsk Polytechnic University Competitiveness Enhancement in the Group of Top Level World Research and Academic Institutions. Project VIU-OEF-66/2019.

References

- [1] Picu R C and Majorell A 2002 Mechanical behavior of Ti–6Al–4V at high and moderate temperatures—Part II: constitutive modeling *Mater. Sci. Eng., A* **326** 306-16
- [2] Gurrappa I 2003 Characterization of titanium alloy Ti-6Al-4V for chemical, marine and industrial applications *Mater. Charact.* **51** 131-9
- [3] Puls M P 2012 *The Effect of Hydrogen and Hydrides on the Integrity of Zirconium Alloy Components: Delayed Hydride Cracking* (Media Springer London Heidelberg New York Dordrecht)
- [4] Patterson E A, Major M, Donner W, Durst K, Webber K G and Rödel J 2016 Temperature-dependent deformation and dislocation density in SrTiO₃ (001) single crystals *J. Am. Ceram. Soc.* **99** 3411-20
- [5] Schulz K, Sudmanns M and Gumbsch P 2017 Dislocation-density based description of the deformation of a composite material *Modell. Simul. Mater. Sci. Eng.* **25** 064003
- [6] Ungár T and Borbély A 1996 The effect of dislocation contrast on x-ray line broadening: a new approach to line profile analysis *Appl. Phys. Lett.* **69** 3173-5
- [7] Dragomir I C, Li D S, Castello-Branco G A, Garmestani H, Snyder R L, Ribarik G and Ungar T 2005 Evolution of dislocation density and character in hot rolled titanium determined by X-ray diffraction *Mater. Charact.* **55** 66-74
- [8] Petrushov S, Ershov V M, Gritsunova K A and Smelsky A 2013 The thin structure of cold-deformed mild steel *Journal of Donbas State Technical University* **39** 141-6 (in Russian)
- [9] Larionov V, Xu S and Syrtanov M 2016 Measurements of hydrogenated titanium by electric methods *AIP Conference Proceedings* **1772** 040005
- [10] Laptev R S, Kudiiarov V N, Bordulev Y S, Mikhaylov A A and Lider A M 2017 Gas-phase hydrogenation influence on defect behavior in titanium-based hydrogen-storage material *Progress in Natural Science: Materials International* **27** 105-11
- [11] Larionov V V, Lider A M and Garanin G V 2015 Eddy current analysis for nuclear power materials *Advanced Materials Research* **1085** 335-9
- [12] Larionov V V, Lider A M, Berezneeva E V and Kh M 2012 Krening, features of the electromagnetic control methods of stratified hydrogen content in construction materials *Appl. Phys. (Prikladnaya fizika in Russian)* **5** 20-4
- [13] Panin A V, Kazachenok M S, Kozelskaya A I, Balokhonov R R, Romanova V A, Perevalova O B and Pochivalov Y I 2017 The effect of ultrasonic impact treatment on the deformation behavior of commercially pure titanium under uniaxial tension *Mater. Des* **117** 371-81
- [14] Umansky I, Skakov Y, Ivanov A and Rastorguev L 1982 Crystallography, X-ray diffraction and electron microscopy *Metallurgy* **632** 351-73 (in Russian)
- [15] Grobovetskaya G P, Nikitenkov N N, Michin I P, Duchkin I V, Stepanova E N, Sypchenko V S 2013 Diffusion of hydrogen in submicrocrystalline titanium *News of Tomsk Polytechnic University* **322** 55-9 (in Russian)
- [16] Ayers J E 1994 The measurement of threading dislocation densities in semiconductor crystals by X-ray diffraction *J. Cryst. Growth* **135** 71-7