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Effects of hydrogen exposure on the mechanical and tribological properties of α-titanium surfaces

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ABSTRACT

The influence of electrolytic hydrogenation on the mechanical properties of the near-surface microstructures of titanium and the resulting tribological behavior (scratch tests and reciprocating ball-on-plane tests) was investigated. Hardening effects of hydrogenation were revealed by nano-indentation methods. Additional quantitative characteristics, such as micro-indentation hardness, Young's modulus, and the work of elastic and plastic deformation, have also been determined. Plastic deformation of surface micro-asperities dominated during the sliding friction of non-hydrogenated titanium. By contrast, brittle fracture and crack formation were observed on hydrogenated surfaces. In a limited number of experiments, the coefficient of friction was reduced by as much as a factor of three after hydrogenation.

A mechanism by which hydrogen affects the tribological behavior of titanium has been proposed. Hydrogen, localized in the dislocation cores, blocks their movement, which leads to hardening of titanium and a reduction in its ductility. During sliding, the periodic external and internal stresses overlap at the contact points, and that leads to micro-cracking and brittle fracture. Evidence for this mechanism remains to be demonstrated in future work.

1. Introduction

Tribological behavior of metals depends significantly on the state and properties of the thin surface layer of a thickness of ~0.1 mm, in which contact processes are localized. During micro-irregularities sliding the stresses appear at the contact points along different directions, which change from the compressive to tensile ones and cause surface damaging [1]. Fracture resistance and character of the damage are determined, first of all, by the micromechanical properties of the surface layers and the work of elastic and plastic deformation of the microirregularities. These values may differ significantly from the mechanical characteristics of the metal macrovolumes as a result of scale effect, adsorption and gases occlusion, hydrogen in particular.

This concerns, to a great extent, the metals which possess getter properties, titanium first of all. It belongs to the group of exothermic metal occluders, which adsorb the hydrogen already at room temperature to form a solid solution and hydride phases [2,3]. With increasing the hydrogen content, the fracture stress in titanium significantly decreases since the hydride transformation has a significant volume effect and causes the increase of the lattice defects and loss of plasticity [4].

The influence of hydrogen on the mechanical properties of titanium surface in the micro-/nanovolumes was evaluated by the nanoindentation and nanoscratch methods. This technique is used on thin films or small volumes of materials to measure mechanical parameters such as Young's modulus, hardness [5], residual stresses [6] etc. Electron microscopy in combination with nanoindentation yields information about local mechanical properties of materials [7].

Changes of the structure and mechanical parameters of the titanium surface layers after hydrogenation determine its exploitation characteristics, especially of the tribological ones. Therefore, the study of the influence of electrolytic hydrogenation on mechanical properties of the metal micro/nanovolumes and its frictional behavior is important for establishing the mechanisms of hydrogen wear and developing the ways of its prevention.

Interconnection between nanomechanical properties and wear resistance of titanium has been investigated by researchers [8]. It was shown that top nanostructured surface layer possesses much better friction properties in comparison with titanium matrix.

The effects of hydrogen on the surface deformation of Ti alloy surrounding nanoindentations are examined in [9]. It is shown that the deformation of the specimen around an indentation depends ambiguously on hydrogen concentration in the metal. At high concentration of hydrogen the pileup decreases.

The aim of this paper is to determine the effect of electrolytic hydrogenation on the mechanical properties of micro/sub-micro-volumes of the surface layers of commercially pure titanium and its tribological behavior.

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2. Experimental technique

Tests were carried out on BT1-0 titanium samples, with chemical composition (in weight percent): Fe, 0.18; C, 0.07; Si, 0.1; N, 0.04; O, 0.12; H, 0.01; and Ti, balance. Specimens of size 40×15 mm^2 each were cut out from the plate of a thickness of 3 mm. Specimens were previously mechanically polished with a diamond paste to a roughness $R_a = 0.63$ μm and annealed in vacuum 10^{-5} Pa and at temperature 950 °C for 60 min for reducing internal stresses and removing dissolved gases.

Hydrogenation was carried out by cathodic charging in the electrolytic solution of 1 N H_2SO_4 plus 10 mg/l As_2O_3 at the room temperature for 1 h. The arsenic trioxide was used for avoiding the H atoms recombination. A lead counter electrode and current density of 1.0, 1.5 and 2/0 A/dm^2 were used.

The concentration of hydrogen in the metal was determined by the local mass spectral analysis on the device ECHO-4M using a laser microprobe-extractor.

To determine the mechanical properties of the surface layers the durometer ПМТ-3 and the method of dynamic indenting were used [10,11]. It is based on the automated recording of the loading curve $P = f(h)$, where P is the load applied to the indenter, h is the depth of its introduction into the investigated material surface. The diamond Berkovich indenter with a three-sided pyramid geometry was used. The angle between indenter axis and a side was 65.03°. The tip radius did not exceed 300 nm.

The main advantage of the method is that the hardness is determined at the time of the tip maximum penetration (h_{max}), i.e. at the beginning of elastic recovery of the material. The curve gives the information about the indenter work needed to overcome the material resistance A_{plast} (area under the loading branch) and the work spent by the material to restore its properties A_{elast} (area under the unloading branch). From these data, the degree of the surface plasticity ε is determined according to the formula: $\varepsilon = (A_{plast} - A_{elast}/A_{plast})$. The value of microhardness by Meyer is found as a ratio of the maximum load P_{max} to the area of the projection dent A, Young's modulus is defined as $E = S/2\sqrt{\pi/A}$, where S is the tangent of the initial unloading curve area.

Moreover, the scratch method was used. This method is based on continuous recording of the friction force at movement of the Berkovich indenter over the surface. The applied load was 1 N and speed of movement – 0.2 mm/s. Indenter stroke length was 2 mm. The method was combined with the determination of the volume of the material displaced by the indenter and the parameters of the roughness of the surface, which was formed at the scratch bottom [12].

The tribological behavior of hydrogenated material under reverse movement by the chart "ball-plane" was studied. The machine for tribological tests was custom-built at Karpenko Physico-Mechanical Institute. Corundum ball (Ø 9 mm) was used as a counterbody. The applied load was 2 N, indenter sliding velocity – 1.6 mm/s, test duration – 2000 s.

Each test was repeated 3–5 times.

Surfaces microstructure was evaluated by the metallographic method using scanning electron microscope EVO 40XVP. The X-ray analysis was carried out using data arrays of X-ray diffraction, obtained by X-ray diffractometer – DRON-diffractography – 2.0M.

3. Experimental results and their discussion

The surface layers of BT1-0 titanium were hydrogenated by cathode polarization with the current density of 1, 1.5 and 2 A/dm^2 for 1 h. The concentration of occluded hydrogen in titanium after hydrogenation with the current density of 1 A/dm^2 was 17.8 ppm, what corresponded to its critical solubility at room temperature and normal pressure. After hydrogenation with the current density of 2 A/dm^2 the hydrogen concentration in titanium rises to 26.8 ppm, thus exceeding the equilibrium solubility by 1.5 times. Under such conditions, the crystal lattice was reconstructed with the formation of the titanium hydride phases. In the X-ray diffractograms the reflexes corresponding to hydride TiH_2 are recorded (Fig. 1). Since the hydride transformation takes place usually at the grain boundaries and is accompanied by the volume effect [13], it initiates the material brittleness. This confirms the considerable scattering of the microhardness (Fig. 2). As seen from Fig. 2 the traditional method of microhardness measuring in the case of hydrogenated titanium proves to be less sensitive and informative. In this regard, to determine the mechanical properties of the metal surface micro/sub-microlayers the method of dynamic indenting was used.

Loading $P(h)$ curves were constructed for titanium in the initial state and after cathode polarization with the current density of 1 A/dm^2 for 1 h (Fig. 3). It was found that as a result of hydrogenation the mechanical properties of the titanium surface layers significantly changed (Table 1). Thus, the growth of internal stresses in the crystal lattice by 19% was observed compared with the initial state. This leads to the increase in microhardness (by Meyer) by 20% and in elasticity modulus by 15%. At the same time the work of material volume recovery after deformation A_{elast} decreases significantly (by 40%).

More information about the characteristics of the titanium surface layers was obtained by the scratch testing.

The scratch testing method, as a single act of friction, allows to evaluate the nature of damage and pressing-out of the material of contact zone between indenter and metal surface. It also can be

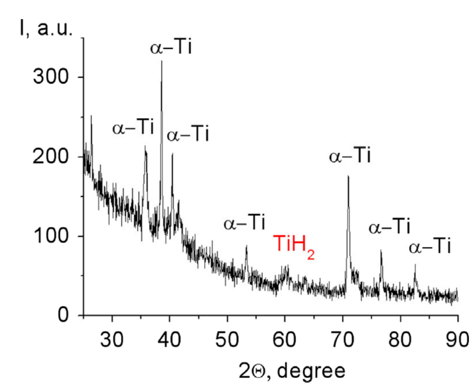

Fig. 1. Diffractogram of the crystal lattice of titanium after hydrogenation with current density of 2 A/dm^2.

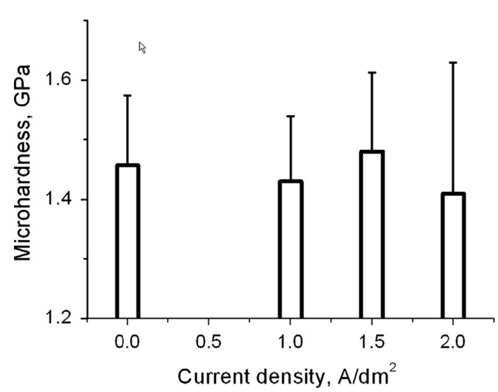

Fig. 2. Microhardness of titanium under different regimes of electrolytic hydrogenation.