



Influence of passive potential on the electronic property of the passive film formed on Ti in 0.1 M HCl solution during ultrasonic cavitation



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ABSTRACT

The influence of the applied passive potential on the electronic property of the passive film formed on Ti at different potentials in 0.1 M HCl solution during ultrasonic cavitation, was investigated by electrochemical impedance spectra (EIS) and Mott–Schottky plot. The influence of the applied passive potential on the structure and composition of the passive film was studied by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The results showed that the applied passive potential can obviously affect the electronic property of the passive film formed on Ti during ultrasonic cavitation. The resistance of the passive film increased, and the donor density of the passive film decreased with increasing the potential. The flat band potential moved to positive direction and the band gap of the passive film moved to negative direction with increasing potential. AES and XPS results indicated that the thickness of the passive film increased evidently with applying passive potential. The passive film was mainly composed of the mixture of TiO and TiO₂. While the TiO₂ content increased with increasing the applied passive potential, and the crystallization of the passive film increased with the increased potential.

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1. Introduction

Cavitation erosion is a serious failure feature of the overflowing components of hydraulic machineries, which attracts many researcher's attention since its discovery. While there is still no effective method or technique used to solve this problem up to now, and the damage caused by cavitation erosion gradually extravagates in many industries, such as in shipbuilding and chemical industry. Initially, the cavities are formed when the pressure falls below the vapor pressure in the low pressure region of flow liquids. The cavities continuously enlarge to form bubbles, and then they violently collapse in the high pressure region. The collapsed bubbles repeatedly send a shock pressure wave or a micro-jet or an acoustic wave through the liquid and onto a material surface to produce plastic deformation crack initiation, crack growth and material removal, resulting in the so-called cavitation erosion phenomena [1,2]. Therefore, cavitation erosion is generally recognized as the result of the mechanical action of shock wave or micro-jet on material surface. Obviously, the key method of eliminating the attack caused by cavitation erosion lies in the surface hardness of the substrate. It is report [3,4] that the silver plated

coating can effectively improve the resistance of cavitation erosion of the substrate. TiN or TiCN coatings manufactured by PVD method have been demonstrated to exhibiting good wear resistance and cavitation erosion resistance [5–8]. Many surface modification processes such as friction stir processed (FSP) [9], laser gas nitriding [10,11] and laser surface alloying [12] have been developed to improve the resistance of cavitation erosion. Although coating and surface modification processes are verified to be effective for enhancing the resistance of cavitation erosion. However, the coatings or the modified surface can not suffer such high and repeating destruction of the micro-jet, even the protection of the coatings or the modified surface on the substrate is unsatisfied due to delamination. Therefore, the most basic way to tackle the cavitation erosion is to improve the cavitation erosion resistance by utilizing the inherent property of the substrate, such as passivity of valve metals or alloys. For titanium and its alloys, the passive film formed on the surface can affect the cavitation erosion resistance according to our previous findings [13,14].

Generally, passivity is a common phenomenon for most valve metals and alloys, such as titanium and its alloy, nickel-based alloy, Nb and Ta, et al. A compact, several nanometer thickness, and highly defective passive film can automatically form on the surface of titanium and its alloys in the existence of oxygen [15–19]. The passive film can be deemed as the ions barrier to protect the

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substrate from further corrosion. However, fewer papers paid attention to the influence of passivity on the cavitation erosion, and there even exists a disagreement about the passivity effect on the cavitation erosion [20]. In order to better understand the role of passive film on cavitation erosion, the passive films are firstly formed at different potentials on titanium in 0.1 M HCl solution during ultrasonic cavitation, and then the electronic properties of the passive films are studied using EIS, MS, photocurrent, AES and XPS, respectively.

2. Experimental

2.1. Sample preparation

The sample is cut from commercial pure Ti (99.99%) manufactured by Bao Ti Group. The working electrode is cut into a wafer with a geometric area of 0.786 cm^2 ($\Phi 10 \times 5 \text{ mm}$), embedded into a two-component epoxy resin and mounted in a PVC holder. The exposed face of the electrode is abraded with 2000-grit SiC paper, polished with $0.5 \mu\text{m}$ Al_2O_3 powder and then cleaned using double-distilled water. The electrolyte is an HCl solution with the electrolyte concentration of 0.1 M.

2.2. Ultrasonic cavitation erosion equipment

Ultrasonic cavitation is produced by a JY92-II DN magnetostrictive-driven apparatus (NingBo scientz Biotechnology Co., Ltd.) resonating at 20KHz with the amplitude of $60 \mu\text{m}$. The schematic of ultrasonic cavitation erosion equipment is showed in Fig. 1. The power of this apparatus is 1KW, and the distance between the top surface of the sample and the horn bottom is about 1 cm.

2.3. Electrochemical measurements

All experiments are performed on an EG&G Model 273A potentiostat/galvanostat with an M5210 lock-in amplifier. A conventional three-electrode system is used, and the counter electrode is a Pt wire. All potentials are measured against a saturated calomel electrode (SCE). Prior to the electrochemical experiment and ultrasonic cavitation, the working surface is reduced potentiostatically to -2.0 V (vs. OCP) for 10 min to remove any oxides.

The passive films are formed on Ti via the following process, firstly, the Ti electrode is passivated at 0.4 V, 0.8 V, 1.2 V, 3 V, 4 V, 5 V, 6 V and 7 V for 2 h in 0.1 M HCl solution during ultrasonic cavitation, then the electrochemical impedance spectra (EIS),

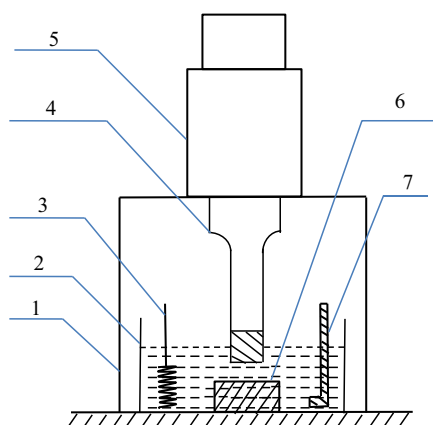


Fig. 1. Schematic of ultrasonic cavitation erosion equipment, 1: sound-proof enclosure; 2: breaker; 3: counter electrode; 4: horn; 5: transducer; 6: working electrode; 7: reference electrode.

Mott–Schottky plots and photocurrent measurements are immediately measured in the static state, respectively.

In which, EIS are performed at the open circuit potential (E_{corr}), a sweeping frequency ranging from 10 kHz to 5 mHz with a potential amplitude of 10 mV is used, the experimental data are analyzed using the ZsimpWin software.

The sweeping potential region of Mott–Schottky plot is in the potential region at -0.6 (vs. SCE) to 1 V, 3 V, 4 V, 5 V, 6 V and 7 V with a 50 mV/s scanning rate, respectively.

The photocurrent measurement is made of a conventional three electrode cell of 1-multi neck flask with a quartz window as a photon inlet, a 1000 W Xenon arc lamp is used as a light source, and a monochromatic light with a wavelength from 250 nm to 380 nm is provided by a scanning digital monochromator controlled by a stepping motor at a scan rate of 2 nm/s. Auxiliary focusing lenses are used to raise the intensity of photons toward the monochromator.

The AES and XPS analysis is carried out with a PHI Quantera ESCA system equipped with an $\text{Al}_{K\alpha}$ (1486.6 eV) source operating at 15 kV and 400 W. The pressure in the analyser chamber is 10^{-9} Torr, and the angle of the sample surface to the detector is set at 90° . The spectrum is calibrated with respect to a C_{1s} value of 284.8 eV. The XPS analysis area is about $2 \text{ mm} \times 2 \text{ mm}$. The surface is etched with Ar^+ ions to obtain depth profiles, the sputter rate is calibrated with SiO_2 and is about 2.2 nm/min.

3. Results and discussions

3.1. Passive performance of Ti in 0.1 M HCl solution during ultrasonic cavitation

Fig. 2 shows the potentiodynamic polarization curves of Ti in 0.1 M HCl solution under static state and ultrasonic cavitation. Obviously, it can be seen that the features of the potentiodynamic curves measured in the static state and ultrasonic cavitation, are mostly similar except the lower passive current density and more negative corrosion potential (E_{corr}) in the case of ultrasonic cavitation. The increased passive current density and negative corrosion potential indicate that the passive property of Ti in 0.1 M HCl solution shrinks under ultrasonic cavitation. The similar phenomenon is observed on 0Cr13Ni5Mo stainless steel in 0.5 M NaCl and 0.5 M HCl solutions [21,22]. It can be also observed that the passive region can be divided into two regions no matter under the condition of static state or ultrasonic cavitation, in which region I is ranging from about 0.2 V to 1.5 V and region II is located in the region above 2 V. The appearance of point a in the potentiodynamic curve may be related to the transition of the film structure and composition [23].

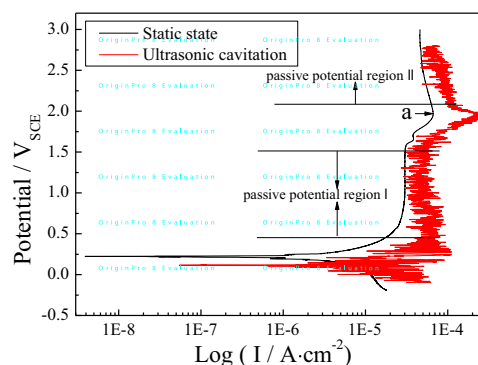


Fig. 2. Potentiodynamic curves of Ti measured in the static state and in the ultrasonic cavitation in 0.1 M HCl solution.

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