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Softening of α-Ti by electrochemically introduced hydrogen

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ABSTRACT

The substantial and permanent modification of the elastic and inelastic properties of α-Ti have been achieved by hydrogen charging with cathodic polarization in an alkaline solution at RT, with the effects being dependent on the hydrogen state of the metal. The decrease in the elastic modulus to values close to those characteristic for bones have been caused by the distortion of the Ti lattice due to the supersaturation of the solid solution with hydrogen and (or) due to the formation of hydride precursors and precipitates. The low, but still detectable decrease in the elastic modulus has been observed by the formation of a compact hydride layer. On the basis of a thorough examination of the effect of cathodic polarization on the formation and morphology of the hydride phase and on the state of the α-Ti lattice, the electrochemical parameters provided: (1) the presence of hydrogen in supersaturated solid solution, (2) the formation of hydride precipitates of various stoichiometry and (3) the formation of the compact hydride surface layer have been determined.

Taking into account the hydrogen induced metal softening, the easiness of electrochemical alloying the metal with hydrogen and no health hazard produced by this element when dissolved in body liquids, the electrochemical hydrogen treatment of Ti implants can be considered as very promising.

1. Introduction

The most important properties for characterizing the materials used for bone implants are: 1) the good chemical compatibility with the bones enabling the deposition of cells and the growth of tissue on the implant surface and 2) the mechanical properties (elastic and plastic ones) as close to those of bones as possible, ensuring the similar behavior of implant and bone under the stress.

Ti and its alloys have been recognized as the most promising metallic materials for implants [1–3]. In order to promote the growth of bone tissue, surface treatments to modify the chemical composition, roughness and porosity of the implant surface have been applied [4,5]. However those treatments, including the formation of Ti oxide layers, do not decrease the hardness and the elastic modulus of the metal. In contrast, the formation of the ceramic surface layers results in an increase in those properties, since the oxides have the higher elastic modulus than α-Ti [1,2,6].

The plasticity of Ti alloys have been found to increase by alloying it with hydrogen introduced at high temperature [7] due to the promotion and the transformation of the low temperature α-Ti phase into the high temperature β–Ti phase of the higher plasticity. Some recent results have shown that hydrogen can also decrease the elastic modulus of α–Ti [8] and hence soften it. However, since the hydrogen solubility in α – Ti is quite low and the hydride is easily formed [9], it is not clear whether hydrogen induced softening occurs due to the intrinsic effect of hydrogen dissolved in the lattice of α-Ti ordue to the formation of the hydride phase having lower hardness [10], or due to the increase in the dislocation density in the metal at the hydride formation.

Hydrogen charging of Ti and Ti-Al intermetallics at ambient temperature has generally led to their embrittlement [9,11]. However, the metal softening due to the electrochemical introduction of hydrogen under the special conditions cannot be excluded.

The maximum solubility of hydrogen occupying the tetrahedral holes in a hcp α-Ti lattice attains 0.2 wt % at 570 K [9,12,13] and decreases to 0.001 - 0.003 wt. % [9,12,14] at RT. At a higher amount of absorbed hydrogen, the TiH_x hydride of the fcc structure is formed [9,12,13,15–17]. An increase in the hydrogen content in this hydride causes the increase in the lattice parameter of hydride from about 4.407 Å at $x = 1.5$ to 4.434 Å at $x = 1.9$ [17] and to 4.44 [9] -4.45 Å [16] at $x = 2$. However, the formation of the tetragonal structure of TiH_2 hydride with the lattice parameters $a = 3.12$ Å and $c = 4.18$ Å has been also reported [13,17,18]. Most studies have shown that hydrogen occupies the tetrahedral holes in hydride [9,12,13,16], but the occupation of both the tetrahedral and octahedral sites (depending on the hydrogen content and temperature) has been also suggested [19].

When α-Ti is exposed to the electrolytes, the formation of the continuous hydride layer [9,14], the hydride precipitates [9,20,21] or the hydrogen dissolution in the metal [22] may occur depending on the solution chemistry and pH, and on the applied potential and time. The hydrogen absorption and the amount of hydride phase increases at an increased cathodic polarization [14,23] and time of charging [21]. In acid solutions, the continuous surface layer of hydride is formed immediately [9,14] at a cathodic current below 5 mA/cm^2 [14]. Cathodic

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charging with a near neutral or alkaline electrolytes causes a lower hydrogen absorption and the formation of the needle hydride precipitates [20]. A decrease in the concentration of the electrolyte also results in a lower hydrogen absorption [23].

A minor change in the arrangement of the parent metal atoms from the hcp lattice of α-Ti to the fcc (or tetragonal) lattice of hydride and the occupation of the similar sites by hydrogen atoms in solid solution and in hydride structure results in an easiness with the solid solution - hydride transformation [12,13]. However, due to the difference in the lattice volume of both phases [17,19] the transformation introduces a stress into the metals [21,24] and hydride [14]. A defect formed in the Ti when the hydride precipitates, provides trapping sites for the hydrogen atoms [22]. Therefore, when the electrochemical hydrogen charging of Ti occurs, the hydrogen may exists as atoms dissolved in an α-Ti lattice, as trapped by defects and as a constituent of hydride phase of various morphology and stoichiometry, differently affecting the elastic and the mechanical properties of the metal. Valuable information on the metal elastic and inelastic properties carried out at a constant frequency at increased temperature provide the internal friction measurements [25]. The measured resonance frequency corresponds to the elastic modulus, whereas peaks formed on the internal friction spectra reveal the activation of certain relaxation process in the metal structure. Therefore, the internal friction measurements permit the study of the effects of hydrogen on the elastic metal properties, on the phase composition and on the interaction of hydrogen with the metal defects [26–28].

Increasing the plasticity of the low temperature α-Ti by introducing hydrogen with electrochemical charging at ambient temperature seems to be very promising. It allows for the treating of the surface of various shapes under precisely controlled conditions, without affecting the bulk material, which may occur at the high temperature. However, considering the softening of α–Ti by the electrochemically introduced hydrogen, the effects of the presence of hydrogen in the various states in metal should be recognized and analyzed.

The electrochemical conditions providing the hydrogen dissolution in α–Ti and the formation of hydride phase have been selected and the effects of those conditions on the morphology and stress state of the formed phases as well as the effects of the modified structure on the elastic and inelastic properties of α–Ti have been studied.

2. Materials and experimental procedures

Samples were cut from a 1 mm thick sheet of Ti of high purity. Since (as mentioned above) the hydrogen absorption is lower in alkaline than in neutral and acid solutions [18,29], the alkaline electrolytes have been selected to provide a lower hydrogen fugacity and therefore enabling to obtain the different states of hydrogen in the metal at subsequently increased cathodic polarization. The nondeaerated 0.1 M NaOH (pH = 11.8) and 2 M NaOH (pH = 13.5) solutions prepared from the NaOH of spectral purity and the double distilled water have been used in this investigation. After polishing, the specimens were immediately immersed into the electrolyte and subjected to cathodic galvanostatic polarization for up to 90 minutes.

The amount of absorbed hydrogen was measured by electrochemical and by thermal extraction methods. In the electrochemical method, the hydrogen was introduced into the metal at constant cathodic polarization and then desorbed by following anodic potentiodynamic polarization [30]. In the thermal extraction method, the amount of hydrogen extracted from the cathodically charged specimens was continuously recorded during the heating process, up to 1200 K at heating rate 5 K/min.

The X-ray diffraction spectra were recorded on a Siemens D5000 diffractometer with $Cu_{k\alpha}$ radiation. The phase composition and the lattice parameters of individual phases were evaluated from the obtained spectra using the JCPDS PDF-2/2001 database [18] and using at least 3 diffraction lines. In the case of hexagonal α-Ti, the parameters ***a*** and ***c*** were calculated using the lines hk0 and 00 l, respectively. The elastic strain of the α-Ti lattice in the direction normal to the specimen surface was calculated as follows:

$$\varepsilon = \frac{d_{\perp} - d_0}{d_0} \tag{1}$$

where: d_0 and $d_{\perp}$– interplanar distance (201) for uncharged and charged α-Ti lattice, respectively.

The internal friction and the resonance frequency were measured at the bending strain mode using a resonance mechanical spectrometer RAK-3 [31]. The specimen (30 × 10 × 1 mm) was mounted in the vacuum chamber with a beam between two electrodes and the sinusoidal voltage was applied to excite the bending oscillation of acoustic frequency. The measurements were done at a strain amplitude of $\varepsilon = 1 \times 10^{-4}$ with heating from 180 K to 800 K at rate of 3 K/min. From the obtained results, the values of the internal friction (Q^{-1}) and of the dynamic Young modulus (E) have been calculated [25,31], respectively:

$$Q^{-1} = \frac{1}{\pi} \ln \frac{A_N}{A_{N+1}} \tag{2}$$

where: A_N and A_{N+1} – the consequent values of amplitude of oscillation.

$$E = 94.68 \left(\frac{l_r}{h}\right)^3 \cdot \frac{m_d}{b} \cdot f^2 \tag{3}$$

where: l_r, h, b and m_d –length, thickness, width and mass of the vibrating part of the sample, respectively; f – the automatically measured resonance frequency.

The Callotte tests [32] were done by rotating a 30 mm ball of bearing steel against the studied surface for up to 24 hrs. The depth of the modified surface layer was calculated from the diameters of formed rings. The ratio of the rings diameter formed on treated surface to that formed on pure Ti (d_H/d_0) was adopted as a measure of the hardness change of the surface layer.

The distribution of elements within the surface layer (depth profile) of the hydrogen charged specimens was characterized using Glow Discharge Optical Emission Spectroscopy (GDOS) [33]. In this method, the topmost layers of specimen are consequently sputtered away, and the released atoms excited by a glow discharge emitted from the radiation being analyzed by optical spectrometer.

The topography and microstructure of the polished Ti seen on the cross-section and on the Callotte rings were observed by optical and scanning microscopy.

It should be strongly emphasized that with all of the tests, with the exception of evaluation of hydrogen charging by the electrochemical method, were done several days after the hydrogen charging. Therefore, the stable effects of hydrogen charging on the structure and the properties of the metal were studied. The mean values of the results obtained for 3 to 5 specimens were taken into account.

3. Results

As seen in Fig. 1a, the polarization curve (II) recorded after cathodic polarization exhibits an anodic current peak not observed on the initial curve (I). A peak is formed due to desorption of the hydrogen which is absorbed with cathodic polarization and its height (Δi_H) corresponds to the amount of absorbed hydrogen [30]. When there is an increase in the cathodic polarization, the height of the anodic peak, and hence, the hydrogen absorption nonmonotonically increases (Fig. 1b). For the more concentrated solution, the Ti absorbs higher amount of hydrogen, especially at the high cathodic polarizations (Fig. 1b). The hydrogen thermal extraction spectra obtained for the hydrogen charged samples reveal a peak at approximately 920 K (Fig. 2a). This peak was formed in 2 M NaOH at the lowest applied polarization and it is higher than that formed in 0.1 M NaOH solution at a similar polarization (Fig. 2b). The