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Evaluation of hydrogen absorption behaviour during acid etching for surface modification of commercial pure Ti, Ti–6Al–4V and Ni–Ti superelastic alloys

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ABSTRACT

The hydrogen absorption behaviour during acid etching for the surface modification of commercial pure Ti, Ti–6Al–4V and Ni–Ti superelastic alloys has been investigated on the basis of the surface morphology, electrochemical behaviour and hydrogen thermal desorption analysis. To simulate the conventional acid etching for the improvement of the biocompatibility of Ti alloys, the specimens are immersed in 1 M HCl, 1 M H_2SO_4 or 0.5 M HCl + 0.5 M H_2SO_4 aqueous solution at 60 °C. Upon immersion, commercial pure Ti absorbs substantial amounts of hydrogen irrespective of the type of solution. In H_2SO_4 or HCl + H_2SO_4 solutions, the hydrogen absorption occurs for a short time (10 min). For Ti–6Al–4V alloy, no hydrogen absorption is observed in HCl solution, whereas hydrogen absorption occurs in other solutions. For Ni–Ti superelastic alloy, the amount of absorbed hydrogen is large, resulting in the pronounced degradation of the mechanical properties of the alloy even for an immersion time of 10 min, irrespective of the type of solution. The hydrogen absorption behaviour is not necessarily consistent with the morphologies of the surface subjected to corrosion and the shift of the corrosion potential. The hydrogen thermal desorption behaviour of commercial pure Ti and Ni–Ti superelastic alloy are sensitively changed by acid etching conditions. The present results suggest that the evaluation of hydrogen absorption is needed for each condition of acid etching, and that the conventional acid etching often leads to hydrogen embrittlement.

1. Introduction

In the biomedical materials field, acid etching for the surface modification of Ti and Ni–Ti alloys is attempted extensively to improve osseointegration [1–7], adhesion to other materials such as resin [8,9] and corrosion resistance [10–12]. The acid etching of Ti alloys is often carried out by immersion in hot HCl and/or H_2SO_4 solutions to obtain high surface roughness, because the surface topography plays an important role in biological interactions at the tissue interface [1]. Moreover, immersion in HCl solutions has been proposed as an excellent decontamination step in surface modification [8]. However, upon acid etching, hydrides often form in commercial pure Ti [4,5,13–16]. Aronsson et al. [17] demonstrated hydrogen thermal desorption from commercial pure Ti subjected to acid etching (HCl + H_2SO_4 solution). There results clearly show that commercial pure Ti absorbs hydrogen during acid etching for surface modification.

Videm et al. [18] reported that thicker hydride layers lead to faster healing and better bone attachment for implants in rabbits. On the other hand, the hydride formation and hydrogen absorption may result in the degradation of mechanical properties, that is, hydrogen embrittlement, of Ti alloys. However, there are no fundamental or quantitative data on the hydrogen absorption behaviour during acid etching for surface modification. Furthermore, the effects of the type of etching solutions on the hydrogen absorption behaviour of Ti and Ni–Ti alloys are unknown.

The hydrogen absorption behaviour is considered to be associated with the electrochemical behaviour. However, we have recently suggested that the amount of absorbed hydrogen cannot be evaluated from only the electrochemical behaviour [19–21]. In particular, for Ti–6Al–4V alloy, the hydrogen evolution does not necessarily lead to hydrogen absorption [20]. Understanding the hydrogen absorption behaviour is useful in the prediction of hydrogen embrittlement or the development of hydride-treated implants. In addition, it is important to examine whether the hydrogen absorption can be predicted from the surface morphology of alloys subjected to corrosion, in order to verify any overlooked hydrogen absorption during acid etching.

The purpose of the present study is to evaluate, by hydrogen thermal desorption analysis (TDA), the amount of hydrogen absorbed during conventional acid etching for the surface modification of commercial pure Ti, Ti–6Al–4V and Ni–Ti superelastic alloys, on the basis of surface morphology and electrochemical

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Table 1
Chemical compositions of tested specimens (mass%).

	Ti	C	H	O	N	Fe	Al	V	Ni
Commercial pure Ti	Balance	0.003	0.0010	0.107	0.003	0.026	–	–	–
Ti–6Al–4V alloy	Balance	0.01	0.0011	0.18	0.01	0.22	6.22	4.1	–
Ni–Ti superelastic alloy	Balance	0.036	–	–	–	–	–	–	55.8

behaviour. The hydrogen thermal desorption behaviour is a promising clue for elucidating the mechanisms of hydrogen embrittlement. Hence, data on the hydrogen desorption behaviour should be accumulated for future study.

2. Experimental procedures

Commercial pure Ti (described previously [19,22]), commercially available Ti–6Al–4V (described previously [20,23,24]) and Ni–Ti superelastic alloys wires with a diameter of 0.50 mm were cut into specimens of 50 mm length. The nominal chemical compositions of these wires are given in Table 1. The surfaces of the specimens were carefully finished with 600-grit SiC paper and ultrasonically cleaned in acetone for 5 min.

To simulate the conventional acid etching in the biomedical materials field, the specimens were immersed in 1 M HCl, 1 M H_2SO_4 or 0.5 M HCl + 0.5 M H_2SO_4 aqueous solution at 60 ± 1 °C for up to 60 min. Corrosion potentials were measured in 200 ml of the test solutions under aerated conditions. The counter electrode and reference electrode used were a platinum electrode and a saturated calomel electrode (SCE), respectively. The measurements of corrosion potentials were started 10 s after immersion in the test solutions. The morphology and surface roughness of the side surface of the specimens subjected to the immersion test was examined by 3D-SEM (ERA-8800; ELIONIX, Tokyo, Japan). The surface roughness R_a and R_z of specimens was measured in each area of $90 \times 120\ \mu m^2$. Standard deviation was calculated from the results of at least three measurements.

The amount of desorbed hydrogen was measured by TDA for the specimens subjected to acid etching (immersion in the test solutions). The amount of desorbed hydrogen was defined as the integrated peak intensity. TDA was performed in vacuum at 10^{-6} Pa using a quadrupole mass spectrometer (ULVAC, Kanagawa, Japan). The measurement was started 30 min after the removal of the specimens from the test solutions. Sampling was conducted at 30 s intervals at a linear heating rate of 100 °C/h.

3. Results and discussion

3.1. Surface morphology

The SEM images of the surface of commercial pure Ti, Ti–6Al–4V and Ni–Ti superelastic alloys immersed in the HCl, H_2SO_4 and HCl + H_2SO_4 solutions at 60 °C for 60 min are shown in Fig. 1. On the side surface of the nonimmersed specimens (Fig. 1(a–c)), scratches due to SiC paper polishing were observed. Upon immersion, the scratches almost disappeared owing to general corrosion irrespective of the type of alloy and solution. The surface morphologies of the immersed specimens depended on the type of alloy and solution. These results indicate that the corrosion behaviour of the alloys is affected by the type of solution.

The 3D images corresponding to the same area in Fig. 1(a–l) are shown in Fig. 2(a–l), respectively. The relationship between surface roughness R_a or R_z of each specimen and the type of solution is listed in Table 2. The surface roughness increased after immersion, but the increase in surface roughness only slightly depended on the type of solution. For Ni–Ti superelastic alloy, the increase in surface roughness was smaller than those of commercial pure Ti and Ti–6Al–4V alloy. The mass and diameter losses (corrosion loss) of each specimen subjected to immersion tests was confirmed using a microbalance and a micrometer caliper, but they were too small to evaluate quantitatively, except for Ni–Ti superelastic alloy immersed in HCl + H_2SO_4 solution. The mass and diameter losses of Ni–Ti superelastic alloy tended to be larger than those of commercial pure Ti and Ti–6Al–4V alloy. Thus, it is unlikely that the small surface roughness of Ni–Ti superelastic alloy is attributed to the amount of mass and diameter losses (the amount of corrosion loss). Ni–Ti superelastic alloy is probably uniformly subjected to corrosion. The origin of the small surface roughness may be the intrinsic corrosion behaviour of Ni–Ti superelastic alloy.

The surface roughness R_a or R_z obtained by the present acid etching was almost consistent with those in previous studies [13]. The osseointegration of commercial pure Ti seems to be improved by the present acid etching. However, it is unlikely that the difference in surface morphology was sufficiently expressed in terms of R_a and R_z. The quantitative evaluation of surface morphology is needed in the future.

3.2. Hydrogen absorption behaviour

For commercial pure Ti immersed in each solution, the relationship between the corrosion potential and the amount of desorbed hydrogen as a function of immersion time is shown in Fig. 3. Similarly, it is shown in Figs. 4 and 5 for Ti–6Al–4V and Ni–Ti superelastic alloys, respectively. The amount of absorbed hydrogen can be calculated by subtracting the amount of desorbed hydrogen of the nonimmersed specimen (0 min) from the amount of desorbed hydrogen.

For commercial pure Ti, the corrosion potential rapidly shifted to a less noble direction after 10–20 min, and then it was stable at approximately −0.6 to −0.7 V_{SCE}, irrespective of the type of solution. In the HCl solution shown in Fig. 3(a), negligible hydrogen absorption was observed in the early stage of immersion. Thus, the hydrogen absorption behaviour does not always correspond to the corrosion potential profile. In contrast, in the H_2SO_4 (Fig. 3(b)) and HCl + H_2SO_4 (Fig. 3(c)) solutions, the rapid shifts in corrosion potential was almost consistent with the start of the increase in the amount of absorbed hydrogen. The increase in the amount of absorbed hydrogen became saturated in the later stage of immersion. The reason for the saturation of hydrogen absorption appears to be the hydride formation in the surface layers of the specimen. This hydride serves as a barrier to further hydrogen absorption [25–30]. The amount of hydrogen absorbed during 60 min was approximately 50–170 mass ppm, and it was in the order of HCl + H_2SO_4 > H_2SO_4 > HCl solutions. It should be noted that the hydrogen absorption occurs even in a short time. Acid etching for a short time leads to an inadequate increase in surface roughness of commercial pure Ti for the improvement of osseointegration. Thus, it is likely that high surface roughness obtained by conventional acid etching was accompanied by substantial amounts of absorbed hydrogen.

For Ti–6Al–4V alloy, the corrosion potential gradually shifted to a less noble direction (−0.2 V_{SCE}) in the HCl solution (Fig. 4(a)); however, no increase in the amount of desorbed hydrogen was ob-