



Surface corrosion enhancement of passive films on NiTi shape memory alloy in different solutions



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ABSTRACT

The corrosion behaviors of NiTi shape memory alloy in NaCl solution, H₂SO₄ solution and borate buffer solution were investigated. It was found that TiO₂ in passive film improved the corrosion resistance of NiTi shape memory. However, low corrosion resistance of passive film was observed in low pH value acidic solution due to TiO₂ dissolution. Moreover, the corrosion resistance of NiTi shape memory alloy decreased with the increasing of passivated potential in the three solutions. The donor density in passive film increased with the increasing of passivated potential. Different solutions affect the semiconductor characteristics of the passive film. The reducing in the corrosion resistance was attributed to the more donor concentrations in passive film and thinner thickness of the passive film.

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1. Introduction

NiTi shape memory alloy is now widely used in biomedical applications due to its special shape memory effect [1], superelasticity [2] and good chemical resistance [3].

The corrosion resistance of the NiTi alloy was significantly increased by laser surface-melted technique in a physiological environment [4]. This was mainly attributed to TiO₂ which contributed to the enhancement of the corrosion resistance and the reduction of nickel ion release for NiTi alloy. In addition, nickel ion release rate also significantly was restrained by laser surface-melted technique. The chemically treated NiTi alloy had good corrosion resistance due to the decrease in surface nickel content and formation of compact titanium oxide [5]. The corrosion resistance of porous NiTi shape memory alloy decreased with the increasing porosity in physiological and Hank's solutions [6]. The study revealed that vapor deposited thin film NiTi shape memory alloy had much higher pitting corrosion potentials and wider passive range than the bulk NiTi alloy [7]. It was suggested that the corrosion behavior of NiTi was much closer to Ti than to Ni, in addition, the high protective character of the passive film formed on NiTi alloy was similar to that of titanium [8]. The oxide formed on the surface of NiTi shape memory alloy by oxidation treatment was similar native Ti oxide [9]. The corrosion resistance of NiTi alloy with the surface nanocrystalline and partial amorphous structure obtained by surface mechanical attrition treatment was significantly enhanced compared to the bare NiTi

with coarse grains in 0.9% NaCl physiological solution, in addition, nanocrystalline and partial amorphous structure promoted early passivation [10]. Grain refinement and amorphization obtained by high-pressure torsion reduced the amount of metallic Ni in the passive films and also increased the thickness of the passive film [11]. The martensitic phase in the austenitic NiTi shape memory alloy improved corrosion resistance and significantly decreased Ni release [12].

Currently, there are some studies about the corrosion behavior of NiTi shape memory alloys, however, there is no comparison study on the corrosion behavior of NiTi shape memory alloy in acid solution, sodium chloride solution and borate buffer solution environments. So, in the present work, this subject has been studied by electrochemical tests.

2. Experimental methods

2.1. Materials preparation

The near-equiatomic NiTi alloy with 50.2 at.% of nickel (nominal composition) was used in this study. The strips of material were solution annealed at 850 °C for 0.5 h and subsequently water quenched.

2.2. Materials characterization

XRD (X-ray diffraction) patterns were recorded by a Rigaku Ultima IV diffractometer XRD-2400 diffractometer, using Cu-Kα radiation at 40 kV and 40 mA. The surface energy dispersive spectra (EDS) of NiTi alloy was characterized by scanning electron microscope (SEM, JSM-6460, JEOL, Tokyo, Japan) instrument.

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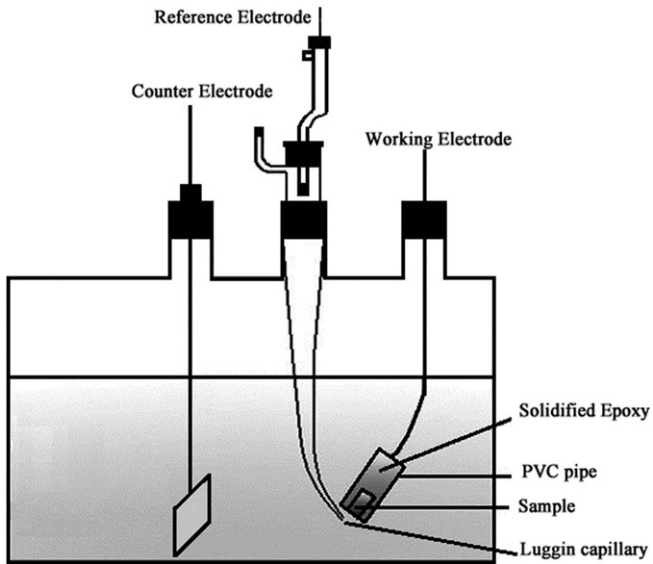


Fig. 1. Schematic diagram of electrolytic cell for electrochemical tests.

2.3. Electrochemical tests

The samples used for electrochemical tests were mounted in epoxy resin, leaving an exposed area around 1 cm^2 in contact with the solution. Prior to any test, all the samples were abraded with 1000, 2000 and 3000 grit silicon carbide paper and polished with $1.5 \mu\text{m}$ alumina slurry. The polished samples were ultrasonically cleaned finally in acetone and ethanol. The electrochemical tests were performed using a CHI Instruments CHI660E electrochemical workstation (Chenhua Instrument Co. Shanghai, China) controlled by CHI version 14.05 software. As shown in Fig. 1, the counter electrode is a Pt foil, and all potentials are measured against a saturated calomel electrode (SCE) connected to the cell via a Luggin capillary. The sample prepared using the above method is used as working electrode. The EIS measurements were carried out using the 100 kHz to 10 mHz frequency range and with a 5 mV amplitude of the AC signal. The resultant impedance spectra were analyzed using the ZsimpWin-V31.

3. Results and discussion

The elemental composition analysis of NiTi shape memory alloy is shown in Fig. 2a. It conforms that the alloy has a chemical compositions of Ni 50.2 at.% and Ti 49.8 at.%. The XRD pattern in Fig. 2b shows that three obvious diffraction peaks at 2θ of 42.3° , 78.2° and 92.8° , respectively, correspond to (110), (211) and (220) lattice orientations of austenite B2 structure in NiTi shape memory alloy. The non-equilibrium

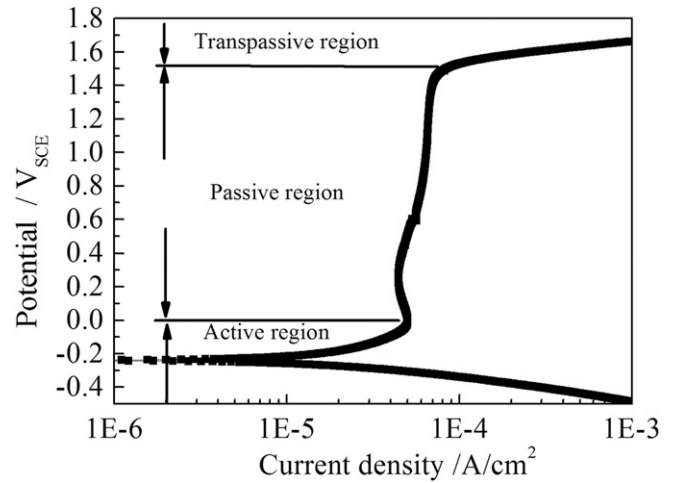


Fig. 3. The polarization curves of the NiTi shape memory alloy in 0.5 M H₂SO₄ solution.

precipitations [13] and martensitic B19' [14] are not observed. In addition, similar preferred grain orientation has been reported.

Fig. 3 shows the potentiodynamic polarization curves for NiTi shape memory alloy in 0.5 M H₂SO₄ at room temperature. The corrosion potential and breakdown potential of NiTi shape memory alloy in 0.5 M H₂SO₄ is $-0.22 \text{ V}_{\text{SCE}}$, and $1.5 \text{ V}_{\text{SCE}}$, respectively. It is obviously seen that the curves are divided into three regions: an active region, a passive region, and a transpassive region. The active region is the region where the metal starts to oxidize by increasing the potential. The oxidation is seen due to an increase in current density. In passive region the metal surface is covered with an oxide film which acts as a barrier between the metal and its corrosive environments. An increase in the potential leads the metal cations to oxidize to a higher oxidation valence, forming a stable passive film. However, the oxidation of metal cations leads not only to higher valence metal cations but also a break down in the passive film and initiating unstable pits. When the current density rapidly increases it comes into the transpassive region and the stable pits appear.

In Fig. 4a, the real impedance is plotted vs. the imaginary impedance at each frequency for NiTi shape memory alloy after being passivated at different potentials in 0.5 M H₂SO₄. It is seen that Nyquist diagrams exhibit a depressed semicircle. The diameter of the capacitive semicircle in the Nyquist plot decreases with the increasing of passivation potential for NiTi shape memory alloy. Bode plots of NiTi shape memory alloy are shown in Fig. 4b. A time constant is observed. The equivalent circuit in Fig. 4c is proposed for fitting EIS data to quantify the electrochemical parameters. In this equivalent circuit, R_s ($\Omega \cdot \text{cm}^{-2}$), R_1 ($\Omega \cdot \text{cm}^{-2}$) and Q (constant phase angle element) represent the resistance of solution, the charge transfer resistance and the capacitance behavior of the passive

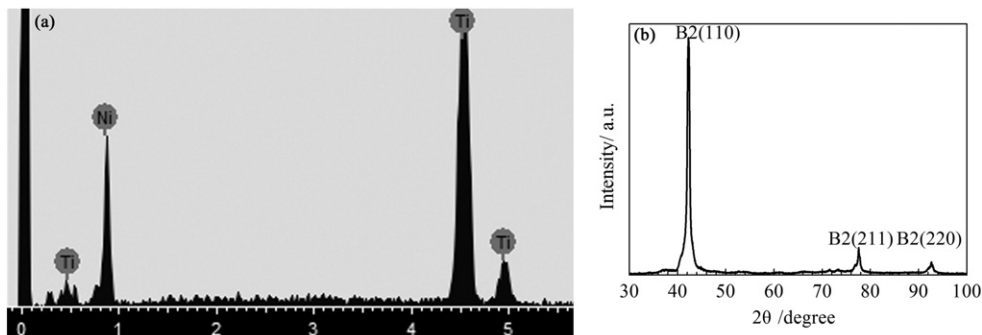


Fig. 2. (a) EDX spectra and the XRD result for NiTi shape memory alloy.

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