

Study of the electrochemical reaction mechanism of nitinol in the methanol-perchloric acid system

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Cyclic voltammetry and polarization curves were used for a study of the electrochemical reaction mechanism of the NiTi alloy in the methanol-perchloric acid system. The anodic polarization curves and the Tafel curves were obtained. The dynamic parameters of the anodic NiTi are: a: 5.0805, b: 1.1958, i_0 : $5.6416 \times 10^{-5} \text{ A/cm}^2$, $n\beta$: 0.048. The results of cyclic voltammetry show that NiTi alloy dissolves in the solution as an intermetallic instead of titanium and nickel separately, and that the anodic reaction of the NiTi alloy in the system is an irreversible process, the anodic peak on the CV curve corresponds to a one-step oxidation process involving seven electrons, and the anodic reaction is $\text{NiTi} - 7e \rightarrow \text{Ti}^{4+} + \text{Ni}^{3+}$ followed by a reduction process $\text{Ni}^{3+} + e \rightarrow \text{Ni}^{2+}$.

Key words: Nitinol, electrochemical reaction mechanism, electropolishing.

Introduction

NiTi shape memory alloy (Nitinol) has been widely applied in different fields such as mechanical engineering, the energy industry and for medical treatments due to its unique shape memory effect, superelasticity, corrosion resistance and biocompatibility [1]. In recent years, the study of Nitinol surface modification has become a "hot" issue. Among those surface treatment methods, electropolishing has attracted a great deal of attention because of its distinctive advantages, but few papers give detailed reports of the mechanism and technique of Nitinol electropolishing due to competitive reasons and a series of technical and theoretical bottlenecks still restrict the applications of Nitinol electropolishing technology [2, 3].

The methanol-perchloric acid system has a comparatively good effect on the electropolishing of NiTi alloy [4]. Cyclic voltammetry and polarization curves were used for the first time for a study of the electrochemical process of the NiTi alloy in this system, and the electrochemical products are analyzed by X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). It is expected that this work will help to expound the electrochemical mechanism and optimize the electropolishing parameters of NiTi alloy.

Experimental

Nitinol sheets were all mechanically polished with successive emery papers down to No.800 (R_a : $0.12 \mu\text{m}$) and pre-electrolyzed to dissolve the original passivation film at 0.7 A/cm^2 (anodic current density) for preparation of the electrochemical study.

The experimental system was composed of an electrode system, a constant potential/current scanning instrument (Wenking PGS81 Potentio-Galvano Scanner) and an X-Y recorder (TYPE 3086). The tri-electrode system was adopted in the electrochemical experiments, i.e., research electrode (Nitinol electrode), auxiliary electrode (stainless steel), reference electrode (saturated calomel electrode).

The composition of the oxide films were investigated with a PHI-610/SAM Auger spectrometer and a PHI-5300 ESCA photoelectron spectrograph.

Results and Discussions

Dynamic parameters

An electrochemical reaction is a special chemical reaction where the electrically-active particles gain or lose electrons on the interface between the electrode and solution. Optimization of the electropolishing parameters depends to a great extent on an investigation of the electrode reaction process and an understanding of the steps, controlling factors, oxidizing or reducing potentials of the electrically-active particles, the reversibility and mechanism of the electrochemical reactions and obtaining quantitative or semi-quantitative data of the reaction rate [5].

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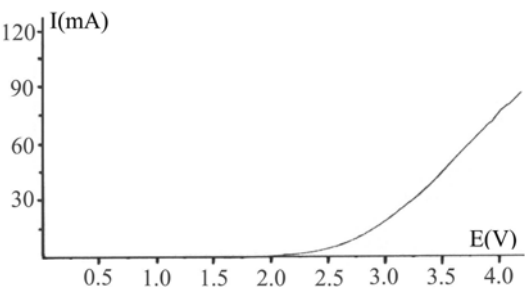


Fig. 1. Anodic polarization curve of a NiTi alloy.

Table 1. Dynamic parameters of a NiTi alloy

a	b	i_0 (A/cm ²)	$n\beta$
5.0805	1.1958	5.6416×10^{-5}	0.048

In this paper, anodic polarization curve of NiTi in the methanol-perchloric acid system is investigated (scanning velocity: 2 mv/s), see Fig. 1. The data from the curve were extracted and given in Table 1.

According to the Tafel equation: $E=a+b\lg i$ [6]
where
 $a: -\frac{2.3RT}{\beta nF} \lg i_0$, $b: \frac{2.3RT}{\beta nF}$ (for anodic polarization),

E: overpotential; i: current density; R: mole gas constant; T: absolute temperature; F: Faraday constant, 96500C/mol; β : symmetrical coefficient of the electrode reaction; n: electron number gained or lost in the electrode reaction; i_0 : current exchange density.

The dynamic parameters of NiTi in the methanol-perchloric acid system can be calculated, see Table 1.

Study of the Electrochemical Reaction Mechanism

Cyclic voltammetry (CV) and polarization curve were used for a study of the electrochemical reaction

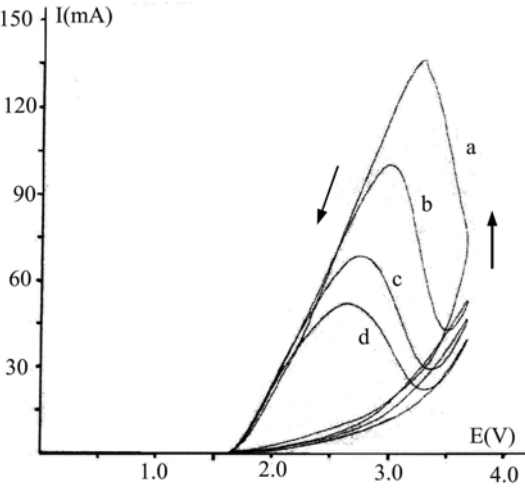


Fig. 2. CV curves of a NiTi anode (scanning velocities: a: 40 mV/s; b: 60 mV/s; c: 80 mV/s; d: 100 mV/s)

Table 2. Effect of scanning velocity on E_{pa} , i_{pa} and $i_{pa}/v^{1/2}$

v (mV/s)	40	60	80	100
E_{pa} (V)	3.26	3.01	2.77	2.64
i_{pa} (mA)	135.2	98.3	67.8	51.2
$i_{pa}/v^{1/2}$	21.38	12.69	7.58	5.12

mechanism of the NiTi alloy in the methanol-perchloric acid system. CV curves of NiTi anode in the methanol- perchloric acid system at different scanning velocities are shown in Fig. 2.

The data from the Fig. 2 were analyzed and E_{pa} (anodic peak potential), i_{pa} (anodic peak current) and current function ($i_{pa}/v^{1/2}$) are shown in Table 2.

It can be seen from Fig. 2 that there is only one anodic oxide peak during the downside scanning on the CV curve without a cathodic reduction peak, which can only be explained that the electrochemical reaction process is an irreversible reaction. The data of Table 2 show, however, that the anodic peak potential declines and the current function declines rapidly with increasing scanning velocity, which is not totally consistent with the reversibility criterion of the electrochemical reaction. Perhaps this is related to the fact that there is no ohmic pressure-drop compensation of the constant potential/current scanning instrument.

To study the dissolution mechanism of the NiTi anode and the reaction type corresponding to the anodic peak of the scanning curve, CV curves of a Ti anode and a Ni anode in the same conditions were tested and typical curves are shown in Fig. 3 and Fig. 4 respectively.

The CV curves of NiTi, Ti and Ni show that the anodic peak of the NiTi CV curve only occurs around

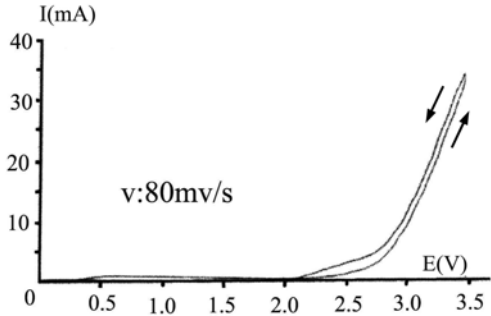


Fig. 3. CV curve of a Ti anode (v: 80 mV/s).

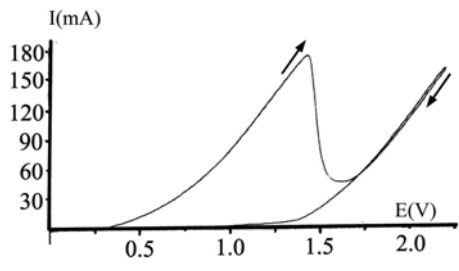


Fig. 4. CV curve of a Ni anode (v: 80 mV/s).

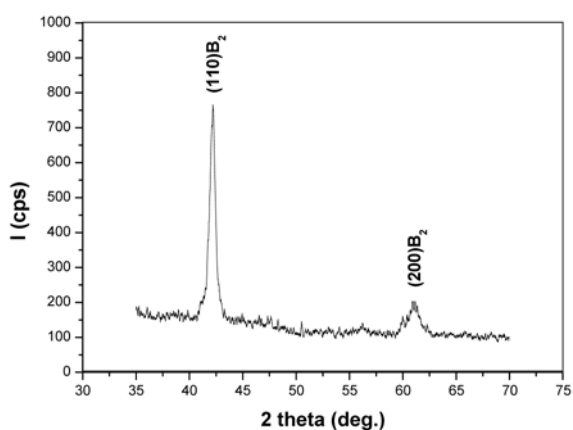


Fig. 5. XRD pattern of a Ti-56wt%Ni alloy.

3V, while that of Ti does not appear during the scanning process and that of Ni occurs around 1.5V. In other words, around the potential where the anodic peak of NiTi occurs, neither Ti nor Ni is subject to the appearance of anodic peaks. This means that the NiTi alloy dissolves in the solution as an intermetallic instead of as titanium and nickel separately.

For validation of the above result, the phase constant of a Ti-56wt%Ni alloy was investigated by X-ray Diffractometry, see Fig. 5. The results show that Ni and

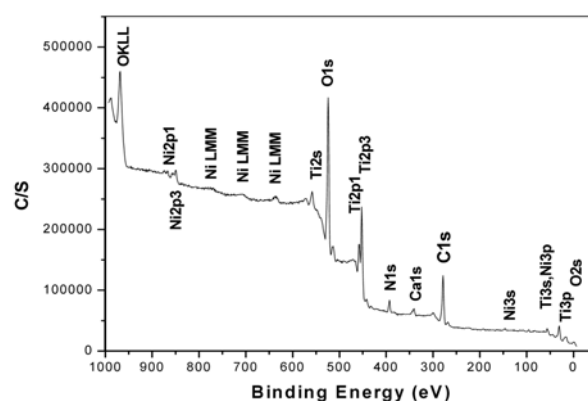


Fig. 6. Complete XPS pattern of a NiTi alloy electrolyzed at constant voltage.

Ti exist as an intermetallic compound, and the phase pattern features only the B_2 parent phase. Analysis of the electrolyte after NiTi electropolishing shows that the ratio between titanium ions and nickel ions approximates to unity, which is consistent with the above conclusion.

After constant-voltage electrolyzing at the anodic peak potential, the NiTi surface was investigated by X-ray Photoelectron Spectroscopy, see Fig. 6 and Fig. 7.

The results show that the ratio of Ti:Ni:O on the

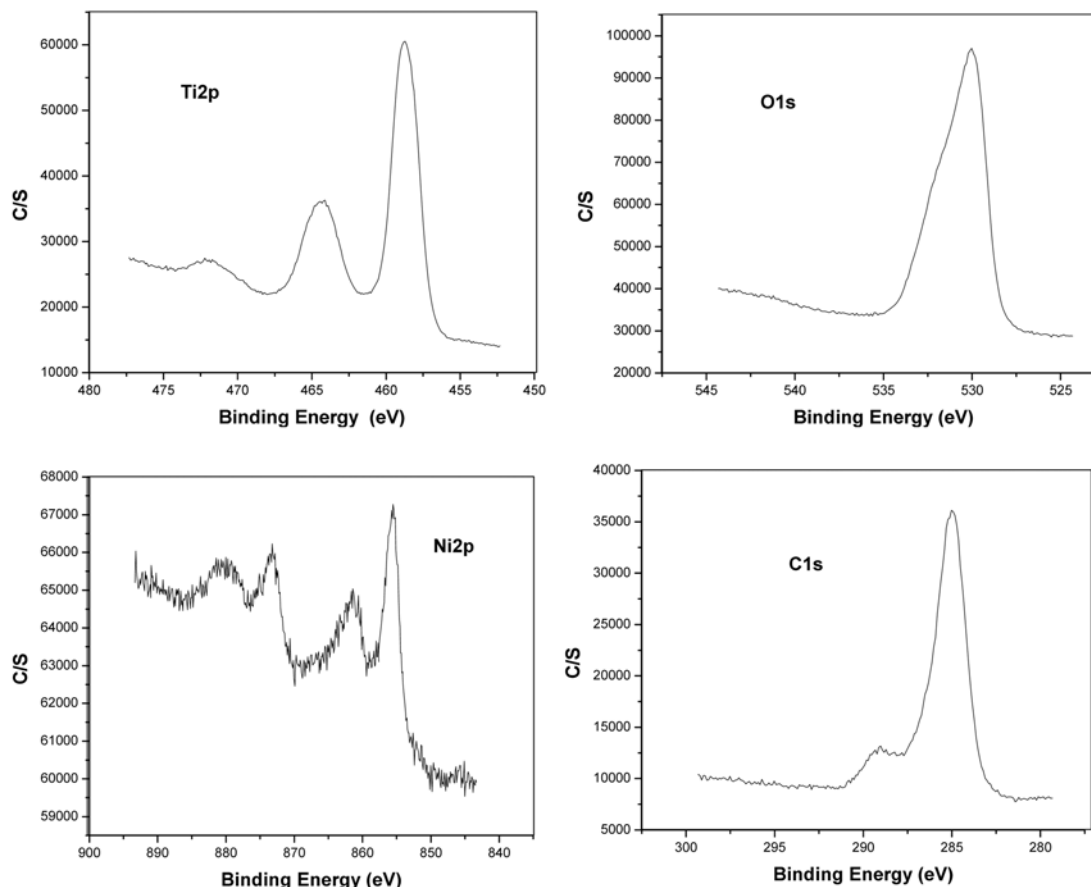
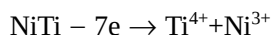


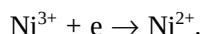
Fig. 7. Different XPS patterns of a NiTi alloy electrolyzed at constant voltage.

constant-voltage electrolyzed NiTi surface is 1:3.98:0.30. The complete XPS pattern of the NiTi alloy electrolyzed at constant voltage is shown in Fig. 6. By snatching peaks of Ni2p, Ti2p, O1s and C1s for magnified observation, the fine structures are shown in Fig. 7, where no distinctive metal state Ni2p peak with a 852.65 eV binding energy or metal state Ti2p peak with a 453.9 eV binding energy could be observed. In other words, the metals Ti and Ni present themselves in the oxidized states, mainly as TiO₂ and Ni₂O₃, or 4⁺ and 3⁺ ionic existences.

Suppose that NiTi alloy dissolves with the same valences as those existing in the anodic surface during the anodic solution process, the anodic peak on the CV curve should occur corresponding to an one-step oxidation process involving seven electrons, and the anodic reaction could be written as:



Since Ni³⁺ is unstable in the acid solution, a reduction process takes place:



This explains why for a certain time after NiTi electropolishing the solution turns green from the color of Ni²⁺ ions.

Conclusions

Cyclic voltammetry and polarization curves were used for the study of the electrochemical reaction mechanism of the NiTi alloy in the methanol-perchloric acid system. Anodic polarization curves and Tafel curves were obtained. The dynamic parameters of the NiTi alloy are: a: 5.0805, b: 1.1958, i₀: 5.6416×10⁻⁵ A/cm², nβ: 0.048. The results of cyclic voltammetry and XPS show that the NiTi alloy dissolves in the solution as an intermetallic instead of as titanium and nickel separately, the anodic reaction of the NiTi alloy in the system is an irreversible process, the anodic peak on the CV curve corresponds to an one-step oxidation process involving seven electrons, and the anodic reaction is NiTi - 7e → Ti⁴⁺ + Ni³⁺ followed by a reduction process Ni³⁺ + e → Ni²⁺.

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