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Electrochemical behavior of Ti-Ni shape memory alloy in fibrinogen solution①

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Abstract: Electrochemical behaviors of Ti-Ni shape memory alloy in fibrinogen solution were studied by electrochemical techniques. The results indicate that the addition of the fibrinogen has no obvious effect on the corrosion potential, but decreases the pitting potential markedly and increases the passive current densities. The analysis of energy-dispersive X-ray for samples adsorbing fibrinogen exhibits that the elements of O, C and N exist on the surface of Ti-Ni alloy. Furthermore, the scanning electron microscope micrographs confirm that the configuration of the adsorbing fibrinogen concentrating on surface defects is like cluster and the fibrinogen adsorption concentration is 96.67 mg/m^2 through ultroviolet ray absorption method. Fibrinogen combined with Ti-Ni alloy surface by complex band and its electrochemical transfer accelerated the corrosion of alloy.

Key words: Ti-Ni shape memory alloy; fibrinogen; electrochemical behavior; adsorption
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1 INTRODUCTION

As a practical biomedical material, Ti-Ni shape memory alloy (abbr. Ti-Ni SMA) is attractive for its special mechanical properties, good corrosion resistance and excellent biocompatibility. However, when the alloy was exposed to blood, its electrochemical properties and biocompatibility were greatly affected by organic components in blood including protein and blood cell. The reaction, such as electrochemical dissolution of the material increasing, coagulation coming into being on the surface and thrombus forming, might occur[1,2]. Researches on implanted metal materials mostly focused on inorganic psychological environments at present[3-5]. There were few reports on the influence of organic compositions on material character. In this paper, the authors investigated the electrochemical properties of Ti-Ni SMA after adding fibrinogen, which proved to have an important effect on coagulation mechanism.

2 EXPERIMENTAL

2.1 Materials and medium

The material employed in this investigation was Ti-Ni SMA. The chemical compositions are that Ti takes up 50.1% (atomic proportion), and the rest, Ni. The conventional tungsten arc-melting technique was employed to prepare the material. Titanium (purity 99.7%), nickel (purity 99.98%) were melted in an argon atmosphere, homogenized at 1 050 ℃ for 72 h, annealed at 800 ℃ for 2 h, and then quenched in water. The elastic modulus is 98 GPa and the yield strength is 200 MPa. Phase transformation temperatures are A_s= 27 ℃, A_f= 56 ℃. The experimental medium was PBS artificial solution, which was produced by analytical reagents and hyperpure water. The compositions are as follows[6]: 8.0 g NaCl + 0.2 g KCl + 1.15 g Na_2HPO_4 + 0.2 g KH_2PO_4 + 1 L H_2O. The pH value was adjusted to 7.4. The fibrinogen solution was prepared by adding lypohilization fibrinogen powder (Sigma) into PBS artificial solution. The concentrations were 0.3 g/L and 3.0 g/L, respectively. The latter is similar to the fibrinogen concentration in human blood.

2.2 Electrochemical measurements

Polarization curves were carried out by a three-electrode system with a scanning rate of 30 mV/min. Electrode potentials were measured with reference to an Ag/AgCl electrode and Pt wire acted as counter electrode. The temperature of the solution was controlled at 37±1 ℃. Once the current density reached 10 A/m^2 during anodic polarization, the potential scanning direction was reversed. If pitting occurred, the potential at which current density rapidly in-

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creased up to 100 μA/cm^2 was defined pitting potential E_b. The potential at the cross point of reversed line and positive direction line was protective potential E_p. Pitting tendency was evaluated by both E_b and E_p values.

2.3 Protein adsorption experiment

Fibrinogen concentration in PBS solution was measured by ultroviolet absorption method. The instrument used to measure was model752 spectrophotometer. The steps of calculating fibrinogen concentration are as follows: first, draw the standard working curves; then computer the equation of concentration by least square method; third, measure the absorbance of samples; finally, calculate the protein concentration from the established concentration equation.

The sample was immerged into 3 g/L fibrinogen solution, which was held at a temperature of 37 ℃, and taken out after 2 h. After rinsed in distilled water, it was deadsorbed in PBS solution for 24 h at a temperature of 37 ℃. Then, the mentioned solution was measured and got absorbance value and adsorption amount. The surface after adsorbing of the sample was analyzed by scanning electron microscope (SEM) and energy-dispersive X-ray(EDX).

3 RESULTS AND DISCUSSION

The time dependence of corrosion potential of Ti-Ni SMA in PBS solution and fibrinogen solution is given in Fig. 1. The corrosion potentials of the alloy moved to positive direction quickly with time firstly, and it tends to stability after 500 min or so. The potential of Ti-Ni SMA, at this time, was around −200 mV. After adding fibrinogen, the potential hardly changed. And to some extent, the corrosion potential can reflect the thermal stability of the same material. Hence, the fibrinogen exerts no obvious effect on the thermal stability of Ti-Ni SMA.

In order to investigate the influence of fibrinogen on electrochemical behaviors of Ti-Ni SMA, samples were polarized in PBS solutions with fibrinogen concentration of 0.3 g/L and 3.0 g/L, respectively. The result is shown in Fig. 2. The passive range was above 800 mV and the preserving current density of the alloy was about 130 mA/m^2. The anodic current density increased markedly with increasing potential. The ring area of reversed scanning curve and forward scanning curve was large, which implied an obvious pitting inclination. After adding fibrinogen, the E_b of Ti-Ni SMA decreased significantly with increasing fibrinogen concentration. The E_b values decreased from 486 mV to 379 mV and 220 mV, respectively, when adding more protein preserving current density value increased largely, while protective potential had

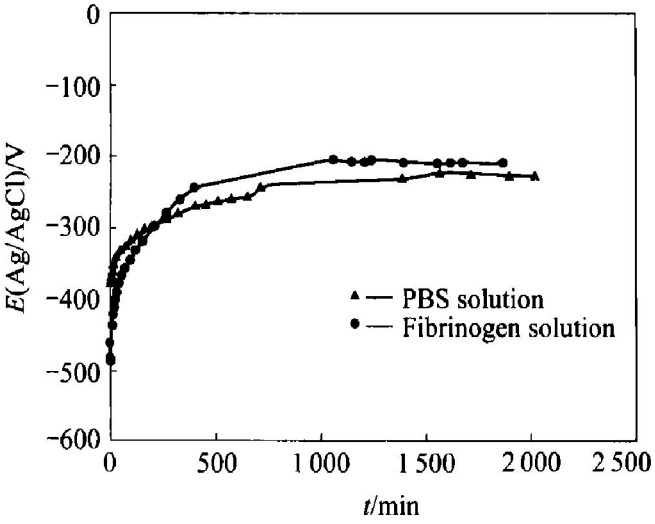

Fig. 1 Curves of corrosion potential vs time of Ti-Ni SMA

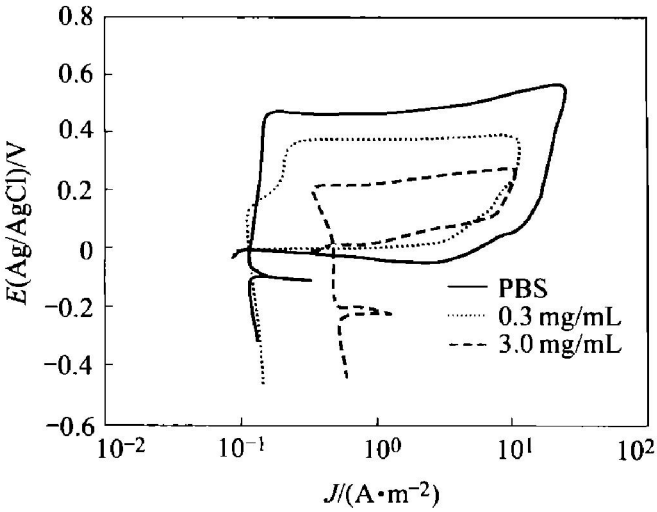

Fig. 2 Effect of fibrinogen on anodic polarization behavior of Ti-Ni SMA

almost no change. It could be explained that the existence of protein accelerated the anodic active dissolution, enlarged the medium erode. The above results are in coincidence with Zabel and Williams et al's results[7, 8].

Fig. 3 shows the EDX result of samples adsorbing fibrinogen for 2 h. Besides Ti, Ni and carbon, nitrogen and oxygen elements were found on the surface of the sample, also. This indicates that the adsorption of fibrinogen occurs. SEM results of fibrinogen adsorption on the alloy surface are presented in Fig. 4. The dispersion of adsorbing fibrinogen was not continuous. The fibrinogen clusters centered on point defect places, which might possess more energy than other points of the surface. This phenomenon may be consistent with the study of GUO et al[9], which reported the discontinuous dispersion of adsorbed fibrinogen on 316L and 317 stainless steel. The fibrinogen amount of adsorption is 96.67 mg/m^2, calculated by ultroviolet absorption method.

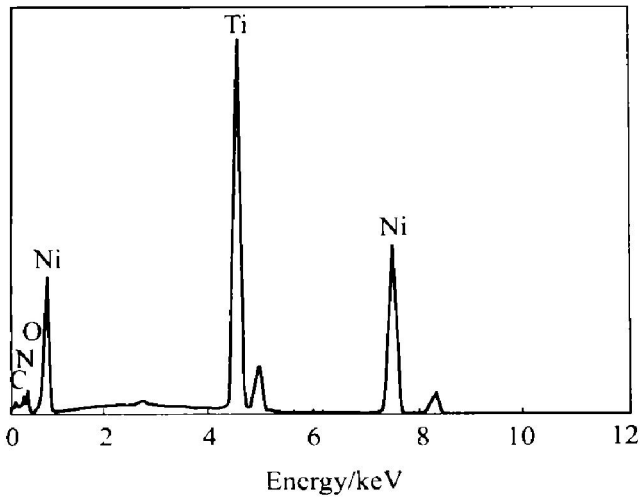

Fig. 3 EDX spectrum of Ti-Ni SMA after adsorbing fibrinogen

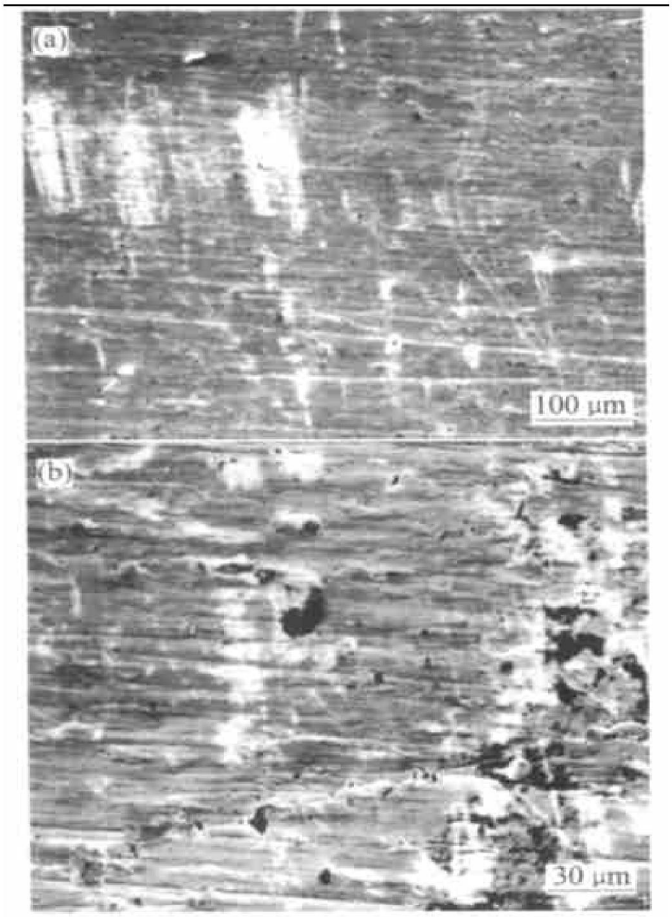

Fig. 4 SEM micrographs of Ti-Ni sample after adsorbing fibrinogen

According to the above experimental results, it could be concluded that the fibrinogen adsorbing on the surface weakened the anodic properties of the alloy. It is mainly found that the pitting breakdown potential was largely reduced. Ti-Ni SMA possesses excellent corrosion resistance, for an oxidation layer coating on the surface, which isolates the medium from matrix and hence prohibits dissolution of the alloy. However, this layer may result in pitting because the layer is brittle and may breakdown at the point where Ti_2Ni phase[10-12] is mixed. Ti and Ni are transition elements, the d electron subgrade of metal ions contains empty electron orbit, which is apt to form stable complex compound with N, C and O elements, which are able to provide lone pair electrons. Clark et al[13] believed that protein could rob metal oxide of metal elements to form complex compound. Therefore, after adding fibrinogen, the complex of fibrinogen and alloy ions was formed on the surface, especially on the defect points, which destroyed passive membrane of Ti-Ni SMA. This complex compound accelerated the metal ions dissolution and inhibited passivation of the alloy. Thus, pitting was apt to occur. Williams et al's research[14] also supported this conclusion.

4 CONCLUSIONS

1) Addition of the fibrinogen has no obvious effect on the corrosion potential of Ti-Ni SMA, but decreases the pitting potential markedly and increases the passive current densities.

2) The analysis of EDX exhibits that the elements of O, C and N exist on the surface of Ti-Ni SMA. The SEM micrographs confirm that the configuration of the adsorbing fibrinogen concentrating on surface defects is cluster and the fibrinogen adsorption concentration is 96.67 mg/m^2.

3) Fibrinogen is adsorbed on the alloy surface by forming complex. Its electrochemical transfer destroys the passive film of Ti-Ni SMA surface and accelerates the corrosion rate of the alloy.

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