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Electrochemical behavior of SUS316L stainless steel after surface modification①

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Abstract: The surface modification for SUS316L stainless steel was carried out by electroplating Rh, ion beam assisted deposition Ta_2O_5 and sol-gel-derived TiO_2. In Tyrode's stimulated body fluid, the surface modified samples were investigated with electrochemical techniques. The results indicate that the electrochemical stability and dissolution are improved significantly after surface modification. Moreover, as to ion beam assisted deposition Ta_2O_5 and sol-gel-derived TiO_2 film, the metal's d orbit electron holes filled up by the oxygen electrons make against the adsorption of hydrogen. Thus the cathode process, which is controlled by the hydrogen reduction, is held back. X-ray diffraction analysis of SUS316L stainless steel after surface modification reveal that each method forms the uniform and compact film on SUS316L stainless steel. These films prevent the dissolving of elements and improve passivation property of the SUS316L stainless steel.

Key words: coronary stent; stimulated body fluid; surface modification; electrochemical behavior
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1 INTRODUCTION

As a metallic implant device, coronary stents need good mechanical performance, wonderful anti-corrosion behavior as well as blood compatible capability for in vivo environments. Nowadays the stents are made by austenitic stainless steel, cobalt-based alloy, titanium and its alloy[1]. Among these materials, SUS316L stainless steel is the most common used one because of its cheap cost, good mechanical behavior and low corrosion rate. It does however, frequently corrode in the body, and release some noxious ions such as Cr, Ni, Mo ions. The ions associate with some adverse biological reactions such as inflammation, thrombosis etc, and lead to infarction in vein[2, 3]. Some researches have proved that such interface reactions can be effectively minimized by surface modification[4-6]. For SUS316L stainless steel, N^+-ion implantation is the common reported method, while others are less discoursed.

In this paper, SUS316L stainless steels are performed surface modification by electroplating Rh, ion beam assisted deposition(IBAD) Ta_2O_5 and sol-gel-derived TiO_2. All these samples are investigated with electrochemical tests in Tyrode's stimulated body fluid.

2 EXPERIMENTAL

2.1 Materials

The examined material was SUS316L stainless steel, whose chemical compositions are listed in Table 1. Before the surface modification, the specimens were wet polished sequentially with 200#, 400#, 600#, 800# and 1 000# silicon carbide (SiC) abrasive paper, degreased in ethanol and acetone solution, rinsed in distilled water, and desiccated in warm air. The working area was 10 mm × 10 mm, while the other area was covered with silica gel.

Table 1 Chemical compositions of specimens (mass fraction, %)

C	Si	Fe	Mn	Ni	Cr	Mo	P	S
0.017	0.60	Bal.	0.91	12.08	17.02	2.01	0.032	0.008

Ingredients of the stimulated body fluid, Tyrode's solution, used for corrosion test, were as follows (g/L)[7]: NaCl 8.0, KCl 0.2, $CaCl_2$ 0.2, $NaHCO_3$ 1.0, $MgCl_2$ 0.1, NaH_2PO_4 0.05. pH of this solution was adjusted to 7.40 ±0.05 and test temperature was maintained at (37 ±1) ℃.

2.2 Electrochemical techniques

A three-electrode electrochemical cell was operated as the anodic polarization test cell. Electrode potentials were measured with reference to an Ag/AgCl electrode and a Pt plate acted as counter electrode. The anodic potentiodynamic polarization measurements were performed on a Princeton Applied Research (PAR) 173' potentiostat at a scan rate of 30

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mV/min. Open-circuit potential was checked by DENKO HA-151 Potentiostat/Galvanostat. The pitting corrosion potential (φ_b) was at which the anodic dissolution current density suddenly increased above a critical potential[8, 9]. The components of surface film were detected by VG ESCALAB MK-2X X-ray Photoelectron Spectroscopy.

2.3 Surface modification on SUS316L stainless steel

2.3.1 Electroplating Rh

The electroplating was carried out at 40 ℃, with a current density of 0.5 A/cm^2 for 1 min. Pt foil acted as counter electrode.

2.3.2 Sol-gel-derived TiO_2

The precursor was Ti(OBu$_4$), EGME as the solvent and acetic acid as stabilizing agent. After being stirred for 30 min, the casting solution was mixed with some ethanol, water and HNO_3. Then a homogeneous and moderate viscosity solution was obtained by further vigorous stirring for 2 h. TiO_2 thin films were deposited on SUS316L stainless steel by immerse-coating technique. Subsequent anneal was performed at 500 ℃ for 1 h.

2.3.3 Ion beam assisted deposition Ta_2O_5

The IBAD apparatus were made by Dalian Maritime University. The background vacuum of the working chamber was 5×10^{-3} Pa and the working gas pressure was 1.7×10^{-2} Pa. The ion bombardment acceleration voltage was 3 000 V and the ion beam current was 40 μA. The flux of oxygen was 2.2 cm^2/min. The argon ions beam assisted voltage was 1 000 V with ion beam current of 20 mA. The working time was 2 h.

3 RESULTS

In Tyrode's solution at 37 ℃, the rest potentials of SUS316L stainless steel and other three different kinds of specimens after surface modification are shown in Fig. 1. From this, it can be seen that the rest potentials of plated-Rh, sol-gel-derived TiO_2 and ion beam assisted deposition Ta_2O_5 specimens are sequential 300 mV, 235 mV and 185 mV more positive than that of SUS316L stainless steel. The results indicate that the surface modifications can improve the thermodynamics stability of the substrate.

Fig. 2 reveals the anodic polarization curves of SUS316L stainless steel without and with surface modification in Tyrode's solution at 37 ℃. According to Fig. 2, the SUS316L stainless steel comes into passive region after slight corrosion during the initial polarization stage. Its passive current density is 8 μA/cm^2. The passive film is destroyed and the polarization current densities suddenly rise after it is positively polarized up to + 640 mV, and then the pitting

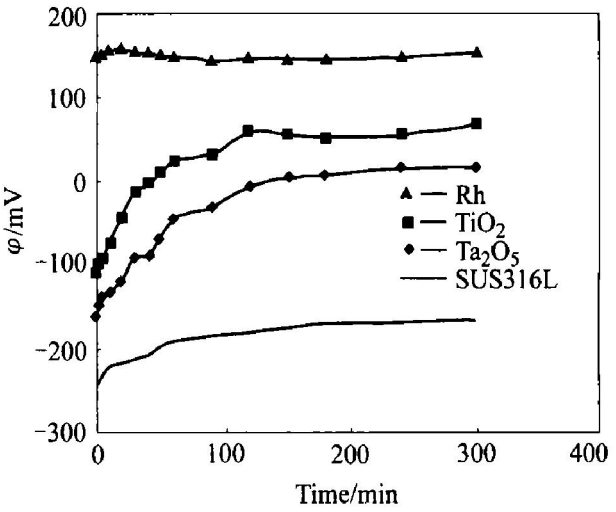

Fig. 1 Corrosion potential vs time curves for SUS316L stainless steel samples before and after surface modification in Tyrode's solution at 37 ℃

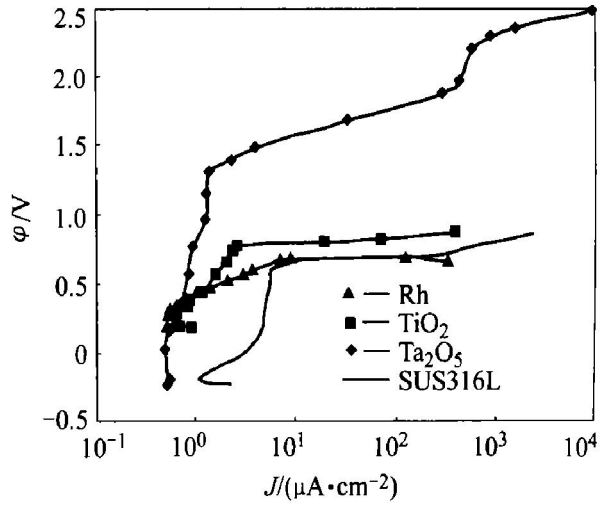

Fig. 2 Anodic polarization curves of SUS316L stain steel samples before and after surface modification in Tyrode's solution at 37 ℃

corrosion happens. Compared to SUS316L stainless steel, the electroplating Rh, ion beam assisted deposition Ta_2O_5 and sol-gel-derived TiO_2 specimens all directly come into passive region from the rest potential. Their passive current densities are respectively 0.5 μA/cm^2, 1.0 μA/cm^2 and 1.0 μA/cm^2. The pitting corrosion potentials (φ_b) of electroplating Rh and sol-gel-derived TiO_2 specimens are + 645 mV and + 750 mV. Whereas ion beam assisted deposition Ta_2O_5 sample's passive region is broad. Even when Cl^- in solution is oxidized to Cl_2 under positive potential more than + 2.0 V, no pitting corrosion is found on the surface. This means that ion beam assisted deposition Ta_2O_5 specimen exhibits the best anode electrochemical behavior, and the sol-gel-derived TiO_2 and electroplating Rh specimens follow then.

The cathode polarization curves of SUS316L without and with surface modification in Tyrode's so-

lution at 37 ℃ are shown in Fig. 3. It can be seen that hydrogen evolves on the surface of SUS316L when the potential is negatively polarized to - 1 100 mV. The reductive potential of hydrogen is - 800 mV on the surface of the electroplating Rh sample. Its reaction current density is higher than that of SUS316L stainless steel. It suggests that electroplating Rh can accelerate the reduction of hydrogen. The cathode hydrogen reduction potentials of ion beam assisted deposition Ta_2O_5 and sol-gel-derived TiO_2 specimens are respectively, - 1 700 mV, - 1 250 mV, which indicates that the two kinds of surface modification hinder the reaction. But the polarizing curve slope of the former is less than that of the latter.

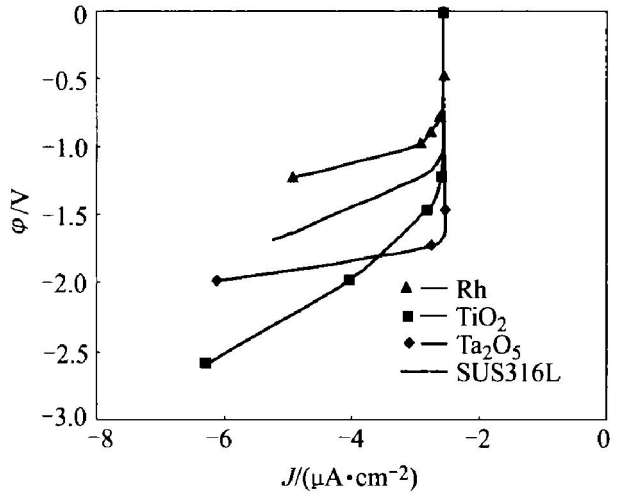

Fig. 3 Cathode polarization curves of SUS316L stain steel samples before and after surface modification in Tyrode's solution at 37 ℃

Fig. 4 shows the XPS analysis of the three surface modified samples. According to Fig. 4(a), the surface is mainly composed of the element Rh, while Fe and Cr are just minim base element. Figs. 4 (b) and (c) indicate that C, O, Ti and Ta are the main elements composed the thin film. Compared with standard spectrum, element Ti is in the crystal formation of TiO_2, and Ta in the amorphous state of Ta_2O_5. C comes from contamination on the surface.

4 DISCUSSION

As the electrochemical tests (Figs. 1 - 3) illuminated, the electrochemical stability and anti-corrosion ability of SUS316L stainless steel in Tyrode's solution are significantly improved after

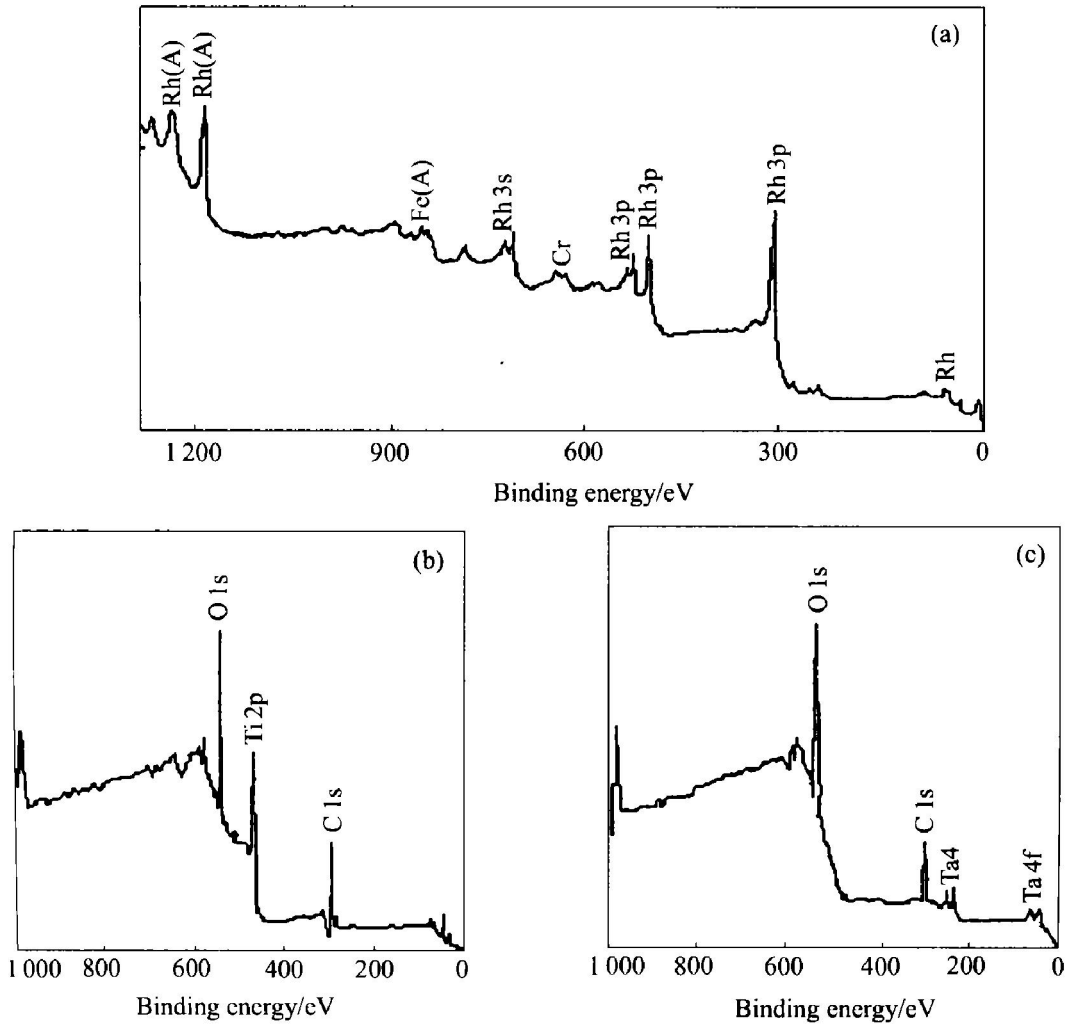

Fig. 4 XPS analysis of SUS316L stain steel after surface modification
(a) —Electroplate Rh; (b) —TiO_2 film by sol-gel method; (c) —Ta_2O_5 film by ion beam assisted deposition

surface modification. Rare metal, Rh, has excellent thermodynamic stability. It results in the sample coated with Rh exhibiting spontaneous passivation at initial potential. Although the passive region of Rh sample is more narrow than that of SUS316L stainless steel, its anti-corrosion ability is superior to the latter. Ion beam assisted deposited Ta_2O_5 film and sol-gel-derived TiO_2 film belong to ceramic films. They present high impedance, which can prevent anode dissolution of substrate metal, positively shift rest potential and improve the electrochemical stability. The X-ray diffraction analysis proves that metal Rh film, Ta_2O_5 amorphous film and TiO_2 crystal film form on the surface after surface modification. Based on the work of LIU[10, 11], those films are uniform and compact, which can mechanically separate substrate from environmental solution and improve the corrosion resistance of the substrate metal. But modification surface films must be assured integrity. Once the substrate is exposed to the environmental solution for the film's lacuna, large cathode and small anode electrochemical couple cell will be formed. It will accelerate the substrate anodic dissolution. That is the reason why the pitting corrosion happens on electroplating Rh and sol-gel-derived TiO_2 specimens.

Different modified surfaces have different influences on the cathode process, especially for the hydrogen reduction. It is reported that the first stage of the hydrogen reduction is hydrogen ions' chemical absorption on the surface. The unfilled d orbit may enhance this process, which catalyzes hydrogen reduction[12]. As to element Rh, its 4d orbit is unfilled and hydrogen ions' chemical absorption is easily achieved. So the hydrogen reductive reaction is accelerated on its surface. Ta_2O_5 and TiO_2 are metal oxides. Because electrons of oxygen fill d orbit of Ta and Ti, which is not beneficial to hydrogen's chemical absorption, hydrogen reductive reaction is hindered.

5 CONCLUSIONS

1) The electrochemical studies carried out on SUS316L stainless steel with and without surface modification, such as electroplating Rh, ion beam assisted deposition Ta_2O_5 and sol-gel-derived TiO_2, show that surface modifications positively shift the rest potentials, decrease the passive current densities, and improve the anodic dissolution property.

2) The cathode process is held up by surface modification. The reason is that electrons of oxygen fill d orbits of Ta and Ti, which hinders chemical absorption of hydrogen.

3) According to X-ray diffraction spectrum of surface modification samples, SUS316L surfaces modified by electroplating Rh, ion beam assisted deposition Ta_2O_5 and sol-gel-derived TiO_2 are respectively composed of Rh, amorphous Ta_2O_5 and crystal TiO_2, which prevents the dissolution of substrate metal and improves their electrochemical stabilities.

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