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Effects of different simulated fluids on anticorrosion biometallic materials ①

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[Abstract] The corrosion behaviors of SUS316L stainless steel, Co-Cr alloy and Ti-6Al-4V alloy in Ringer's, PBS(-) and Hank's solutions have been investigated. The results indicate that the corrosion of Ringer's solution is the strongest, then followed by PBS(-) and Hank's solution. The presence of HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-} and glucose in the PBS(-) and Hank's solution probably reduces the corrosion inhibitor and corrosion current. The decrease of the solution's pH significantly increases the corrosion rate and susceptibility to localized corrosion of SUS316L SS and Co-Cr alloy. However, Ti-6Al-4V alloy exhibits an exceptional stability and has only a slight increase of corrosion rate with decreasing pH.

[Key words] simulated body fluids; biomedical material; corrosion; corrosion inhibition
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1 INTRODUCTION

Corrosion is one of the most important reasons for the failure of metallic biomaterials implanted in human body. Researching the implanted metals' corrosion should consider many factors, such as the properties of the materials, the composition of the body fluids, the change of pH value, the interaction between the implants and the surrounding tissues. Because of the complexity of the human physiological environment, it is difficult to perform a test in body. Therefore, varieties of simulated body fluids are often used to experiment in vitro.

Most of the previous studies[1~4] on implant materials have focused on the corrosion resistance of some materials in one solution. Fewer studies have examined the influence of the components and pH of the solution on the corrosion behavior of the biomaterials. This study investigated the effects of the components of simulated body fluids and the change of pH on the corrosion behavior of SUS316L SS, Co-Cr alloy and Ti-6Al-4V alloy in Ringer's, PBS(-) and Hank's solutions respectively.

2 MATERIALS AND METHODS

The examined materials are SUS316L stainless steel, Co-Cr alloy and Ti-6Al-4V alloy, whose chemical compositions are listed in Table 1.

All the specimens are in the same dimension (10 mm × 10 mm × 2.5 mm) with a working area of 1 cm^2. The samples were wet polished sequentially with 200-, 400-, 600-, 800- and 1000-grit silicon carbide (SiC) abrasive papers, and then degreased in acetone, rinsed in distilled water, dried in warm-air.

Table 1 Chemical composition of materials examined (mass fraction, %)

Materials	C	Si	Fe	Mn	Ni
SUS316L	0.019	0.71	Rem	0.97	12.08
Co-Cr alloy	1.04	0.64	2.43	1.63	2.48
Ti6Al4V	0.004	–	0.16	–	–
Materials	**Cr**	**Mo**	**Al**	**W**	**V**
SUS316L	17.43	2.15	–	–	–
Co-Cr alloy	29.78	–	–	3.92	–
Ti6Al4V	–	–	6.45	–	3.81
Materials	**P**	**S**	**Co**	**Ti**	**N**
SUS316L	0.027	0.011	–	–	0.027
Co-Cr alloy	< 0.01	< 0.01	Rem	–	–
Ti6Al4V	–	–	–	Rem	0.004

To simulate body fluids, the Ringer's solution[5], PBS(-) solution[6] and Hank's solution[5] were used. Their ingredients are listed as follows (g/L):

Ringer's solution, NaCl 8.5, KCl 0.2, $CaCl_2$ 0.2, $NaHCO_3$ 0.2;

PBS (-) solution, NaCl 8.0, KCl 0.2, Na_2HPO_4 1.15, KH_2PO_4 0.2;

Hank's solution, NaCl 8.0, KCl 0.4, $CaCl_2$ 0.14, $NaHCO_3$ 0.35, $C_6H_{12}O_6$ 1.0, $MgCl_2\cdot 6H_2O$ 0.1, $MgSO_4\cdot 7H_2O$ 0.06, Na_2HPO_4 0.06, KH_2PO_4 0.06.

In order to investigate the influence of pH, all the solutions were sequentially adjusted to pH (7.20

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±0.5), pH(5.50 ±0.05), pH(3.50 ±0.05), and the temperature of the solutions was maintained at (37 ±0.5) ℃.

A three-electrode electrochemical cell was used as the anodic polarization test cell. Electrode potentials were measured with reference to a saturated calomel electrode (SEC) and 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 mV/min. The corrosion rate was tested by weak-polarization techniques.

3 RESULTS AND DISCUSSION

3.1 Effect of composition of simulated body fluids on polarization behavior of biomaterial

Fig. 1 shows the anodic polarization curves of the specimens in different simulated body fluids at pH 7.2. According to Fig. 1(a), the titanium alloy had almost the same protection potentials, passive regions and repassivation potentials in the three solutions. The only difference is that the passive currents in Hank's and PBS(−) solutions are slightly lower than that in Ringer's solution (Fig. 1(b)). The potentials at which the current densities take a sudden increase show some deviation. From Figs. 1(a) and (b) another important fact is both the titanium alloy and the Co-Cr alloy have no hysteresis loops when the potential scan is reversed, which illustrates that the two alloys keep a balance between passivation and dissolution of the passive films. On the contrary, the SUS316L SS comes about obvious hysteresis loops in three solutions (Fig. 1(c)), and the curves suffer a significant effect by the solutions. The breakdown potential, which is + 285 mV in Ringer's solution, rises in the noble direction (+ 356 mV vs SEC) in Hank's solution. The protection potential also changes from − 10 mV to + 7 mV, and the passive current density then decreases from 2.570 μA/cm^2 to 1.778 μA/cm^2.

The corrosion rates of the materials tested by the weak-polarization method are listed in Table 2. It can be proved by the data that for all the materials the corrosion rates in Ringer's solution are the highest, then followed by those in PBS(−) solution and those in Hank's solution.

The results indicate that the corrosiveness of the solutions is different according to the difference of composition. The Ringer's solution is the strongest corrosive, then followed by the PBS(−) and Hank's solutions. The variety may well be due to the additives (Na_2HPO_4 and KH_2PO_4), in PBS(−) and Hank's solutions but not in Ringer's solution.

It has been reported that HPO_4^{2-} and $H_2PO_4^-$ ions could be absorbed on the surface of metal, and form a film of $Mn^+_{(OX)}\cdot H_2PO_4^-\text{(ads)}\cdot xH_2O$ or $Mn^+_{(OX)}\cdot HPO_4^{2-}\text{(ads)}\cdot xH_2O$ or $Mn^+_{(OX)}\cdot PO_4^{3-}\text{(ads)}\cdot xH_2O$[7,8], which may restrain the anodic actions. Since PBS(−) and Hank's solutions have the similar influence on the polarization behavior of all the materials as shown in Fig. 1, we could confirm that Na_2HPO_4 and KH_2PO_4 acted as an inhibitor for the corrosion of the materials.

Hank's solution, however, is a more complex simulated body fluid than PBS(−) solution. It addi-

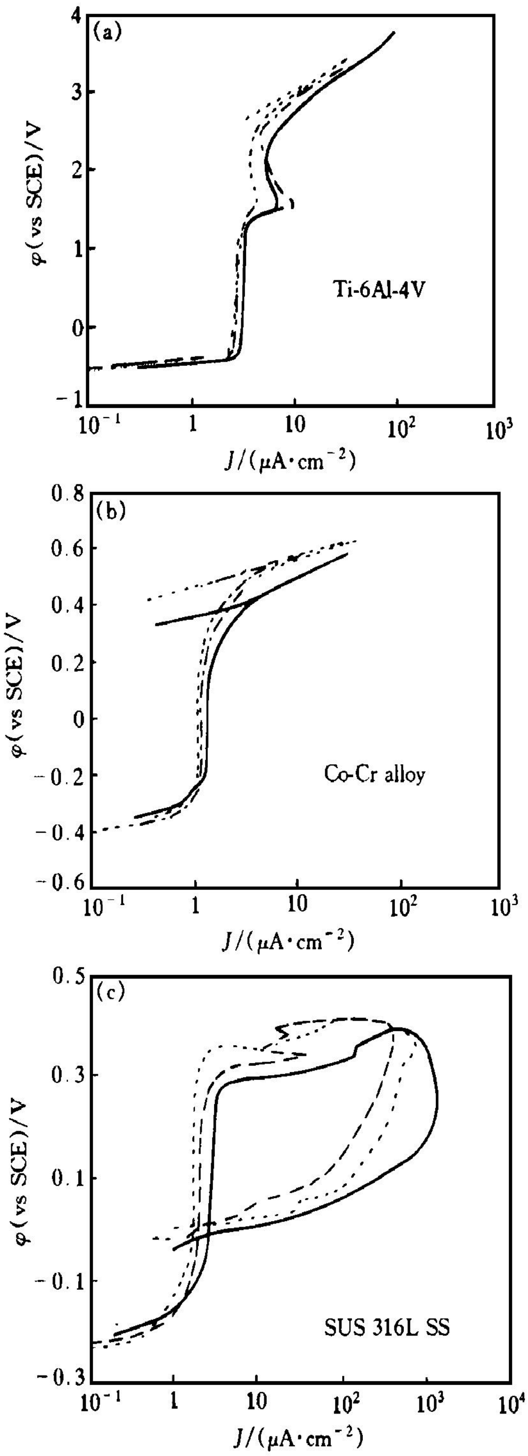

Fig. 1 Anodic polarization curves of materials in simulated body fluids (37 ℃)
1 —Ringer's solution; 2 —PBS(−) solution; 3 —Hank's solution

Table 2 Corrosion current densities of materials examined in different simulated body fluids at 37 ℃ (nA/cm^2)

Material	Ringer's solution pH7.2	Ringer's solution pH5.5	Ringer's solution pH3.5
316L SS	39.68	86.43	124.72
Co-Cr alloy	29.47	62.27	97.54
Ti-6Al-4V	38.13	58.5	76.45

Material	PBS(-) solution pH 7.2	Hank's solution pH 7.2
316L SS	33.24	29.59
Co-Cr alloy	28.88	23.05
Ti-6Al-4V	31.31	24.8

tionally possessed glucose, SO_4^{2-} ion and other elements and ions existing in body fluid. Due to the corrosion resistance of SO_4^{2-} ion and glucose[9], its corrosiveness further decreased. Because the composition of the body fluid, which consists of varieties of proteins, organic acids, alkaline metal ions and inorganic salts, is even more complex than that in Hank's solution, the implanted materials show a sophisticated corrosion behavior in vivo. It has been proved that the corrosion rate of implants in vivo is lower than that in simulated body fluids[10]. Other studies claimed that the proteins in vivo greatly increased the dissolution for Co, Cu and made a slight increase for Cr, Ni but not affected Al and Ti[11].

From an engineering point, the corrosion current densities of the above materials are very low, which ranged between 20 nA/cm^2 and 40 nA/cm^2. But the quality evaluation to the implanted materials considers that the probable tissue reaction could not be avoided unless the corrosion rate is below 0.01 mpy[12], which in stainless steel is equivalent to a corrosion current density of about 30 nA/cm^2 if a valence of 3 is assumed. So it is necessary to recover the effect of each ingredient in body fluid to decrease the corrosion to a lower extent.

3.2 Effect of pH

Fig. 2 illustrates the effect of pH on the anodic polarization curves of the materials. It is obvious that the polarization curves of Ti-6Al-4V changed only a little with the undulation of pH from 7.2 to 3.5. However with the reduction of pH, the passive current density of Co-Cr alloy increases, and corrosion potential becomes positive. Under the same conditions, the pitting potentials and protection potentials of 316L SS become negative, which makes it more sensitive to local corrosion such as pitting corrosion.

The corrosion current densities of the materials in Ringer's solution adjusted to various pH values are

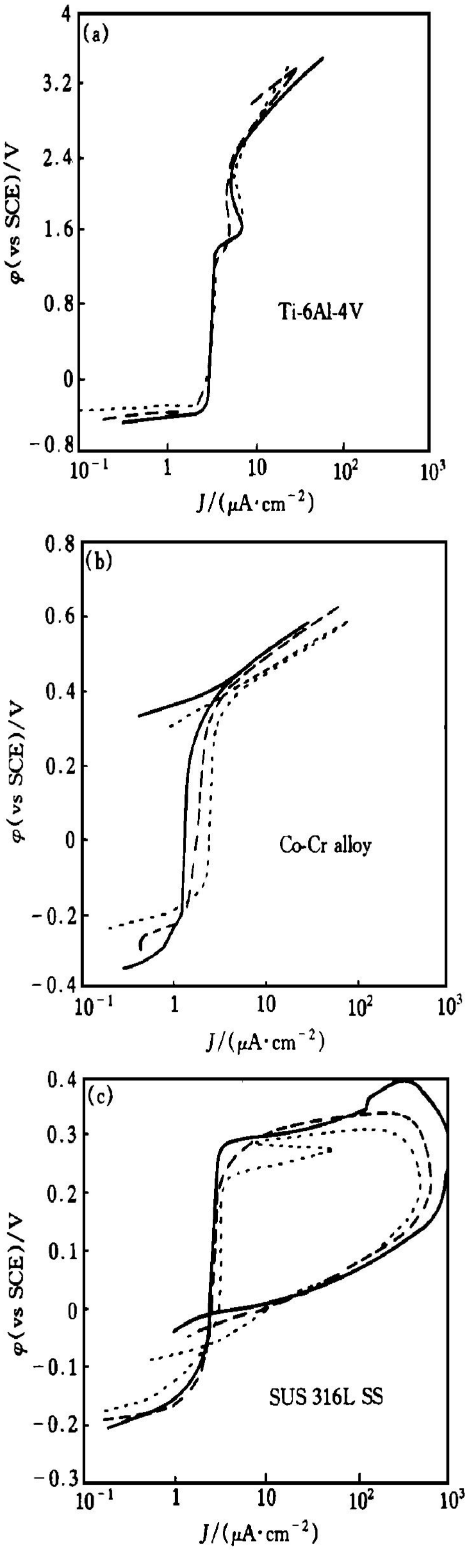

Fig. 2 Anodic polarization curves of tested materials in Ringer's solution with different pH values
1—pH= 7.2; 2—pH= 5.5; 3—pH= 3.5

listed in Table 2. Apparently the corrosion current densities of all the specimens increase for the reduction of pH. To 316L SS and Co-Cr alloy, the corrosion current densities increase from 39.68 nA/cm^2 to 124.72 nA/cm^2 and 29.47 nA/cm^2 to 97.54 nA/cm^2 respectively as the pH decreases from 7.2 to 3.5. The Ti-6Al-4V alloy includes a small change in corrosion current from 38.13 nA/cm^2 to 76.45 nA/cm^2 as the pH decreases from 7.2 to 3.5.

Surgeons and infections can always bring about a local or complete acidic circumstance in body. Furthermore, because of the features of metallic corrosion, the pH in body fluids around the implants may equally make a decrease. The decrease of pH has a great influence on the anticorrosion of biomaterials and promotes their susceptibility for the local corrosion, which eventually results in the release of the hazardous metal ions and causes the corrosion failure of the implants.

So, we should pay enough attention to the effects of pH on the corrosion behavior of implanted materials.

4 CONCLUSIONS

1) The corrosiveness of the three simulated body fluids appears to be different with the sequence of Ringer's > PBS(−) > Hank's solution.

2) HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-} ions and glucose added into the artificial fluids benefit the biomaterials against corrosion.

3) The reduction of pH increases the susceptibilities of 316L SS and Co-Cr alloy, and accelerates the release of the metallic ions as well. However, Ti-6Al-4V alloy only get a little influence from the reduction of pH.

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