

One-Step Synthesis of TiO₂-Hydroxyapatite Nano-films on NiTi Alloy by Hydrothermal Method

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Abstract: NiTi alloy was subjected to one-step hydrothermal treatment in the concentrated CaHPO₄ and Ca(H₂PO₄)₂ solutions for bioactive surface modification. Results show that the treated samples are covered by films composed of fine grains (~70 nm) and large particles (100~250 nm). X-ray photoelectron spectroscopy analysis indicates that Ti at the surface presents as TiO₂, Ni is not detectable, and Ca and P exist in the form of calcium phosphate. X-ray diffraction peaks of anatase TiO₂ and hydroxyapatite are presented for the treated samples. Potentiodynamic polarization test in a Ca-free Hank's balanced solution reveals that the treated sample has a markedly improved corrosion resistance compared with the polished sample. The present work would provide a one-step bioactive surface modification method with easy-operation, relatively low processing temperature and less corrosion, and potentially suitable for biomedical porous NiTi alloy.

Key words: NiTi alloy; hydrothermal; TiO₂; calcium phosphate; hydroxyapatite

NiTi alloy has potentially wide biomedical applications due to its shape memory effect, super-elasticity, good biocompatibility, low modulus (~60 GPa, vs 110 GPa of titanium), etc. The high elastic modulus of orthopedic implants will lead to the problem of 'stress shielding', retarding rehabilitation of the impaired bone. In order to reduce elastic modulus of metallic implants, porous titanium, NiTi and other alloys are being developed^[1-3], and their bioactive surface modification becomes an interesting topic in recent years.

Although the well-known alkali-heat treatment can induce surface bioactivity for titanium and its various alloys^[4-6], it has drawbacks in surface modification of porous titanium metals. The corrosion of alkali solution was reported to have an adverse effect on porous titanium, resulting in deteriorating the mechanical properties^[7]. Heat treatment can alter the microstructures of special alloys, e. g. NiTi alloy^[8], and TiNb alloy^[6], thus varying their mechanical properties. Therefore, methods with relatively lower processing temperature and less

corrosion effect have to be developed for surface modification of porous NiTi alloy and other special titanium alloys.

Hydrothermal treatment is an easily-operated and lower processing temperature method for surface modification of Ti, NiTi and other Ti alloys. Less corrosive solutions of calcium hydroxide, CaCl₂ and MgCl₂ were used for hydrothermal growth of calcium compound or Ca/Mg containing TiO₂ films on titanium to improve its bioactivity^[9-13]. The shortcomings of these methods are that the solutions still have a corrosion effect on titanium during the hydrothermal treatments, and the as formed films contain only Ca or Mg, without phosphate.

In the present work, NiTi alloy was modified by a one-step hydrothermal treatment in less corrosive calcium phosphate solutions in the context of bioactive surface modification of porous titanium metals. The surface structure, the chemical composition and the corrosion resistance of the treated alloy samples were investigated.

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1 Experiment

The nearly equiatomic NiTi alloy sheet with a thickness of 2.0 mm was wire-cut into small pieces (size 10 mm × 10 mm) used for samples, then they were polished, ultrasonically cleaned in acetone, ethanol, deionized water in sequence, and dried in air. The polished samples were hydrothermally treated in deionized water, 10 mmol/L CaHPO₄ · 2H₂O or Ca(H₂PO₄)₂ solution (sample SA, SB, SC, respectively). The filling ratio of solution in the Teflon-lined autoclave was ~80%. The samples stood vertically in the autoclave with the help of titanium clamps. The autoclave was sealed and heated at 200 °C for 24 h. After the treatment, the samples were evacuated and rinsed with deionized water for several times and dried.

Surface morphologies and elemental composition of the samples were analyzed with a scanning electron microscope (SEM, FEI Quanta 600F) equipped with the energy dispersive analysis of X-ray (EDX), and crystallography was examined by X-ray diffraction (XRD, Cu K α , X'Pert PRO). Elemental composition and chemical bonding states of the samples were examined by X-ray photoelectron spectroscopy (XPS, Al K α , K-Alpha, VG).

The corrosion resistance of the alloy samples was evaluated by potentiodynamic polarization tests in a Ca-free Hank's balanced salt solution (HBSS, NaCl 8.00 g/L, KCl 0.40 g/L, NaHCO₃ 0.34 g/L, KH₂PO₄ 0.06 g/L, Na₂HPO₄ · 12H₂O 0.12 g/L) by an electrochemical workstation (Model CS150, Corrtest[®]) at ambient condition. A platinum electrode was used as counter electrode, and the saturated calomel electrode (SCE) was reference electrode.

2 Results and Discussion

2.1 Surface morphology and elemental analysis

Surface morphologies of the hydrothermally treated NiTi alloy samples are shown in Fig.1. Sample SA is covered by a dense film composed of nano-particles (~70 nm) and a few nano-platelets. TiO₂ nano-grains can be hydrothermally prepared on Ti substrate through a dissolution-precipitation mechanism^[9]. Sample SB has small grains as well as large particles (100~250 nm) at the surface. Similar morphology is

observed for sample SC, but the particles are not even at the surface. By assuming spherical shape of the nano-particles, the film thickness of samples SB and SC can be estimated to be around 100~200 nm. Ca and P elements were detected by EDX for samples SB and SC. The large particles at their surface are presumed to be calcium phosphate. Water contact angles of the three samples are 98.8°, 69.6° and 79.7°, respectively. The smaller contact angles of samples SB and SC are possibly due to the formation of hydrophilic calcium phosphate grains at the surface.

Surface chemical composition of sample SB was examined by XPS analysis, with the Ti 2p, Ca 2p, P 2p and O 1s spectra shown in Fig.2. Titanium at the sample surface presents mainly in the form of TiO₂, having the binding energies of 464.4 eV (Ti 2p_{1/2}) and 458.6 eV (Ti 2p_{3/2}). The flat Ni 2p spectra indicate that Ni is absent at the surface, even after 20 s sputtering (not shown). The Ca 2p peaks (350.8, 347.2 eV) and P 2p peak (133.3 eV) confirm that calcium phosphate is formed at the sample surface^[14]. According to the studies on hydrothermally treated Ti^[10,11], calcium compounds (titanate, carbonate or hydroxide) can also be formed in Ca²⁺-containing solutions. In the O 1s spectra, the main peaks at 530.0/529.8 eV are attributed to TiO₂. The peak related to calcium phosphate (531.1 eV^[14]) lies in the left shoulder area. The small peak of hydroxyl groups is positioned at even higher bonding energy (532.0 eV).

2.2 Crystallography analysis

Glancing-angle XRD patterns of samples SB and SC are shown in Fig.3. The diffraction peaks of the alloy substrate as well as small peaks are ascribed to anatase TiO₂ and hydroxyapatite ($2\theta = 31.6^\circ$) are presented, especially for the sample SB.

During hydrothermal treatments of titanium in water, nanostructured TiO₂ films are formed on the substrate through a dissolution-precipitation mechanism^[9,12]. The nano-particles in Fig.1a are suggested to be TiO₂. When alkaline-earth metal ions are presented in the aqueous system of hydrothermal treatment, titanates will be synthesized^[9]. The formation of CaTiO₃ may provide nucleate sites for calcium phosphates^[13]. For NiTi alloy hydrothermally treated in CaHPO₄ solution

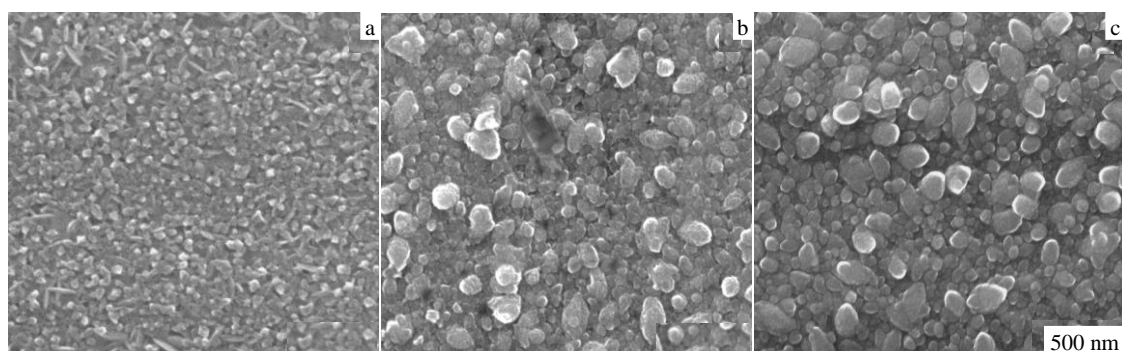


Fig.1 SEM micrographs of the hydrothermally treated NiTi alloy samples: (a) SA, (b) SB, and (c) SC

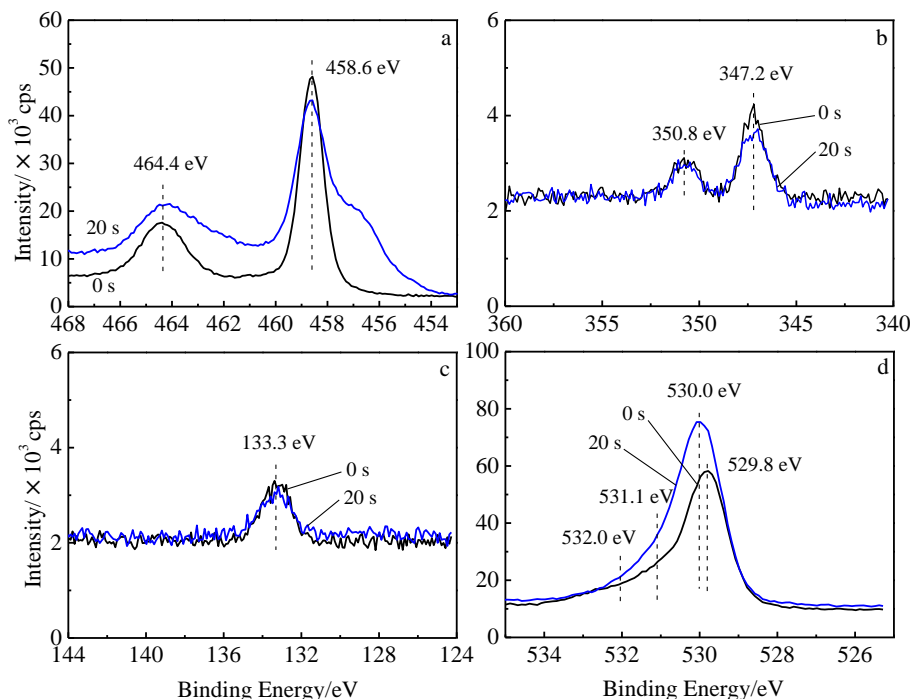


Fig.2 XPS spectra of NiTi sample SB without or with 20 s sputtering: (a) Ti 2p, (b) Ca 2p, (c) P 2p, and (d) O 1s

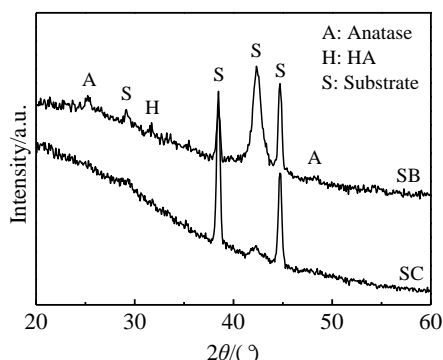


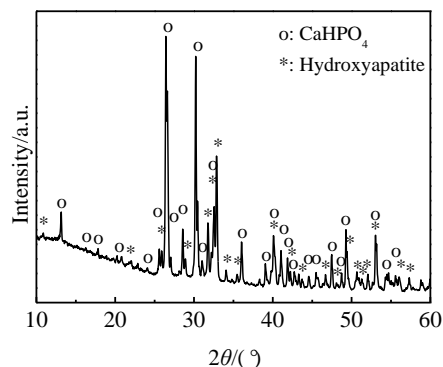
Fig.3 Glancing-angle XRD patterns of the NiTi samples

(sample SB), diffraction peaks of anatase TiO_2 and hydroxyapatite are detected. To further confirm calcium phosphate phases of the surface layer, 50 mmol/L $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ solution was hydrothermally treated at 200°C for 24 h, washed and dried at 80°C for overnight. XRD pattern of the obtained powder in Fig.4 shows that CaHPO_4 is partially transformed to hydroxyapatite. This is consistent with the report that hydroxyapatite nano-crystallites can be prepared by hydrothermal hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\beta\text{-Ca}_3(\text{PO}_4)_2$ [15]. Therefore, the large particles in Fig.1b and 1c are determined as hydroxyapatite nano-crystallites.

2.3 Corrosion test

Corrosion resistance of the NiTi samples was tested by potentiodynamic polarization in the Ca-free HBSS solution

(Fig.5). The polished sample has a slightly higher corrosion

Fig.4 XRD pattern of the powder obtained by hydrothermally treating 50 mmol/L $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ solution at 200°C for 24 h, washed and dried at 80°C for overnight

potential (E_{corr}), but larger corrosion current density (I_{corr}) than the hydrothermally treated sample SB (Table 1). After a range of anodic polarization, the passive current becomes relatively stable and pitting occurs ($E_{\text{pit}} = 0.55 \text{ V}$). The heterogeneous microstructure, e.g. precipitate phases, may play roles in the pitting behavior of NiTi alloy. For the hydrothermally treated sample SB, the passive current density is much smaller (I_{pass} , $\sim 1/71$), and the pitting potential is higher than that of the polished. This demonstrates that the hydrothermally grown TiO_2 -hydroxyapatite film has effectively improved corrosion resistance of NiTi alloy, which is beneficial for its

biocompatibility.

In the present work, hydrothermal treatment of NiTi alloy

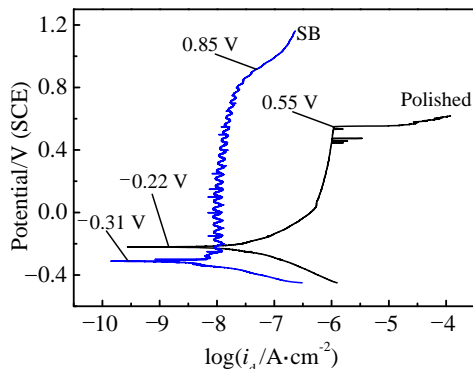


Fig.5 Potentiodynamic polarization plots of the polished and the treated sample SB

Table 1 Corrosion data of the NiTi alloy samples

Sample	$I_{corr}/\mu\text{A cm}^{-2}$	E_{pass}/V	$I_{pass}/\mu\text{A cm}^{-2}$
Polished	0.032	1.37	0.855*
SB	0.005	1.11	0.012*

*: Value at the middle potential of the passivation range, E_{pass}

was carried out in less corrosive calcium phosphate solutions. The modified NiTi alloy with TiO_2 -hydroxyapatite nano-films has undetectable Ni at the surface and the corrosion resistance is markedly improved, and thus it is expected to possess better biological properties. This one-step hydrothermal method is the one with easy operation, low processing temperature and less corrosion, and potentially applicable to bioactive surface modification of porous NiTi alloy.

3 Conclusions

1) Small nano-grains (~70 nm) and large particles (100~250 nm) are formed at the surfaces of hydrothermally treated NiTi alloy.

2) Ti at the surface presents as TiO_2 , Ni is not detectable,

and Ca and P are in the form of calcium phosphate. Anatase TiO_2 and hydroxyapatite are detected for the treated alloy samples.

3) The treated sample has the markedly improved corrosion resistance compared with the polished sample.

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采用水热方法在镍钛合金表面一步合成 TiO_2 -羟基磷灰石纳米薄膜

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摘要: 采用高浓度的 CaHPO_4 和 $\text{Ca}(\text{H}_2\text{PO}_4)_2$ 溶液对镍钛合金进行一步水热处理, 以进行生物活性表面改性。经过处理的试样表面覆盖的薄膜由小晶粒 (约 70 nm) 和大颗粒 (100~250 nm) 组成。X 射线光电子能谱分析表明试样表面的钛以 TiO_2 形式存在, 检测不到镍, 钙磷元素以磷酸钙存在。处理试样检测到锐钛矿 TiO_2 和羟基磷灰石的 X 射线衍射峰。在无钙 Hank's 平衡盐液中的动电位极化实验表明, 处理试样的耐蚀性比抛光试样大大提高。本研究提供的一步法生物活性表面改性方法易于操作, 处理温度低, 腐蚀性弱, 可用于生物医用多孔镍钛合金的表面改性。

关键词: 镍钛合金; 水热; TiO_2 ; 磷酸钙; 羟基磷灰石

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