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ARTICLE

Hydrothermal Surface Modification of a Low Modulus Ti-Nb Based Alloy

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Abstract: A low modulus near β type titanium alloy (Ti-25Nb-3Zr-2Sn-3Mo, or TLM alloy) was subjected to hydrothermal treatments with a urea solution at different temperatures followed by heat treatment. The surface structure, the chemical composition, adhesion and hydrophilicity of the treated TLM alloy were investigated by SEM, XRD, XPS, Rockwell-C indentation test and contact angle measurement. The results show that nanosheet films of ammonium titanate can be formed at 105 and 120 °C, while the nanoparticle film of anatase TiO_2 containing Nb_2O_5 is formed at 150 °C on the alloy surface. The subsequent annealing heat treatment at 400 °C can decompose the ammonium salts and crystallize titania. The obtained oxide films have a good adhesion. The duplex treatment has enhanced the hydrophilicity of the TLM alloy, and it would be good for its biocompatibility.

Key words: titanium alloy; biomaterials; hydrothermal; TiO_2; hydrophilicity

As a material for hard tissue implants, titanium has a good corrosion resistance and an excellent biocompatibility, but its elastic modulus (110 GPa) is much higher than that of bone (1~30 GPa). The mismatch of elastic modulus will lead to 'stress shielding', retarding rehabilitation of the impaired bone. Therefore, low modulus alloys has been developed, which are mainly Ti-Nb based β or near β type titanium alloys[1-4], e.g. Ti-25Nb-3Zr-2Sn-3Mo alloy (or TLM alloy, elastic modulus 60 GPa).

For orthopedic and dental implants, titanium can form a nanoporous titanate film by alkali treatment, which can induce the formation of bioactive apatite layers both *in vitro* and *in vivo*, based on which Kokubo proposed the concept of 'bioactive metals'[5]. Moreover, *in vivo* tests demonstrated that the sodium removal treatment could effectively improve the early bone-implant interface resistance to a shear force[6,7]. Particularly, the thermal treatments at above 600 °C were used to remove sodium partially as well as crystallize and strengthen the porous titanate film[8]. For the titanium alloys whose structure and properties are thermally sensitive[3,4], the methods with relatively lower processing temperatures have to be developed to remove the cationic ions of the alkali treated surface layer. In this work, TLM alloy are hydrothermally treated with a urea solution and then annealed at a lower temperature of 400 ℃. The surface structure, the chemical composition, the adhesion and the hydrophilicity of the treated TLM alloy samples were investigated.

1 Experiment

The TLM alloy sheet with a thickness of 0.6 mm was supplied by Northwest Institute for Nonferrous Metal Research, China. The sheet was sparkle-cut into small pieces (size 10 mm×10 mm×0.6 mm). Pure Ti plates (grade TA2, size 10 mm×10 mm×1.2 mm) were also used for comparison. The plates were polished, ultrasonically cleaned in acetone, ethanol, deionized water in sequence, and dried in air. The polished metal plates were hydrothermally treated in 1 mol/L solution of urea, which was prepared by dissolving urea (analytically pure) in deionized water. The solution was filled in a Teflon-lined autoclave, with the filling ratio of 70%. The au-

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toclave with the metal plates was sealed and heated at 105, 120, 135, 150 and 170 ℃, respectively, for 24 h. The treated samples were soaked in deionized water overnight, and dried in air. Some samples were then heat-treated at 400 ℃ for 30 min in air.

The surface morphologies of the samples were observed by scanning electron microscopy (SEM, FEI Quanta 600F), and crystallography was analyzed by X-ray diffraction (XRD, Cu Kα, Rigaku D/MAX-2400). The elemental composition and the chemical bonding state of the samples were examined by X-ray photoelectron spectroscopy (XPS, Al Kα, VG). The spectra were calibrated relatively to C 1s peak (E_b=284.8 eV) resulting from adventitious hydrocarbon present on the sample surface. Rockwell-C indentation test was used to assess the mechanical properties of the surface layers of the samples[9]. The tip curvature radius of the indenter of the tester (TCY-A) was 200 μm, and the loading rate was ranged between 9.2×10^{-4}~2.8×10^{-1} mm/min during the test. The hydrophilicity of the samples was assessed by water contact angle measurement, which was done by injecting 5 μL deionized water at the sample surface with a contact angle goniometer (JY-82, Dingsheng Test Machines Co. Ltd., China) under ambient conditions. Some samples were subjected to UV illumination treatment (wave length centered at 253 nm) to increase the hydrophilicity.

2 Results and Discussion

2.1 Surface morphology observation

The surface morphologies of the hydrothermally treated TLM alloy and Ti samples are shown in Fig.1. Dense nanoporous film is formed on Ti105 (denotes 105 ℃ heat treated) sample. The film is relatively thin revealed by the apparent scratches. The similar nanosheet film on Ti hydrothermally treated at 105 °C is composed of ammonia titanate[10]. For TLM samples, only sparse nanofibers are observed at 105 °C, but a complete nanoporous film is formed at 120 °C. Some nanoparticles are formed in the nanoporous films of Ti120 (denotes 120 ℃ heat treated) and TLM135 (denotes 135 ℃ heat treated) samples, and the particles grow bigger and cover the substrates at 150 °C. The nanoparticles of TLM150 (denotes 150 ℃ heat treated) sample have a size of 160 nm, much larger than that of Ti150 sample and even of Ti170 (denotes 170 ℃ heat treated) sample (60 nm and 120 nm, respectively, Table 1).

2.2 Crystallography analyses

XRD patterns of the hydrothermally treated and the heat treated TLM alloy samples are shown in Fig.2. No additional peaks are observed for the TLM sample hydrothermally treated at 120 °C. The absence of diffraction peaks of ammonia titanate[10] (niobate) seems to be due to the small thickness of the nanosheets or amorphous nature of the film shown in Fig.1f. TiO_2 diffraction peaks are still not observed for TLM135 sample. A small peak appears at 2θ=25.2° for the sample hydrothermally treated at 150 °C. This peak can be ascribed to anatase TiO_2, but the monoclinic phase of Nb_2O_5 is not ruled out due to its various standard diffraction patterns (ICDD #37-1468, #27-1311, #20-0804, etc). The crystalline phases formed at 150 °C correspond to the nanoparticles illustrated in Fig.1 h.

During the hydrothermal treatment, Ti surface was dissolved in the urea solution to form ammonium titanate[10], and the ammonium salts could be gradually decomposed by dehydration and hydrolysis to form titania nanocrystals[11]. The high temperatures (≥150 °C) accelerate the second reaction.

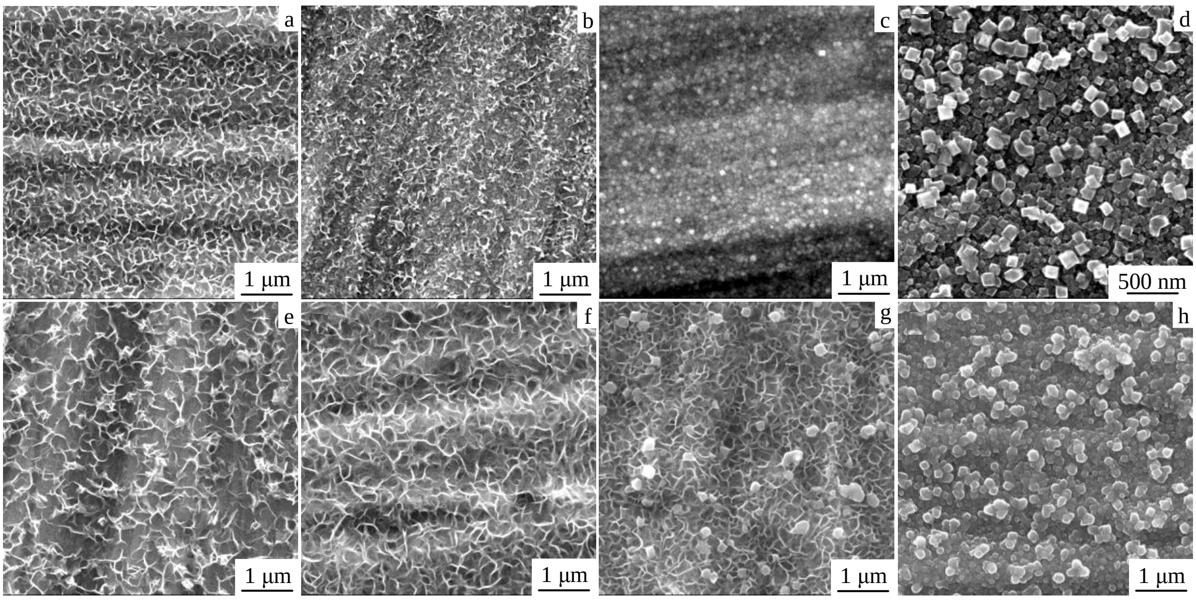


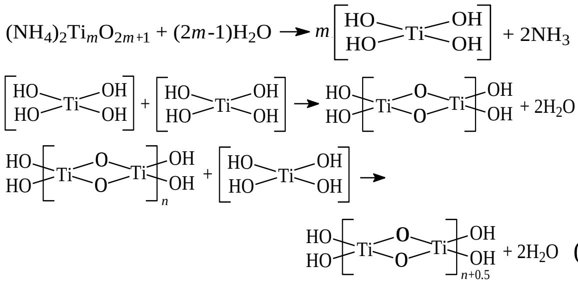
Fig.1 SEM images of the TLM alloy and Ti samples hydrothermally treated at different temperatures: Ti: (a) 105 °C, (b) 120 °C, (c) 150 °C, (d) 170 °C; TLM: (e) 105 °C, (f) 120 °C, (g) 135 °C, and (h) 150 °C

Table 1 Particle size of the hydrothermally treated TLM and Ti samples

Samples		Particle size/nm
Ti150		40~80
Ti170	Up	110~140
	Down	50~90
TLM135		120~170
TLM150	Up	150~180
	Down	80~100

The probable reactions are as follows:

$$m\mathrm{Ti}+2\mathrm{NH_4OH}+(2m-1)\mathrm{H_2O}\rightarrow(\mathrm{NH_4})_2\mathrm{Ti}_m\mathrm{O}_{2m+1}+2m\mathrm{H_2} \quad (1)$$



(2) (3) (4)

In TLM alloy (Ti-25Nb-3Zr-2Sn-3Mo), compared with Ti, the element of Nb is easier to react with hot alkali solution to form niobate salts[2]. Soluble niobate salts (e.g. $K_8Nb_6O_{19}\cdot 10H_2O$) are firstly formed, and insoluble niobate salts (e.g. $KNbO_3$) are then formed at 150 °C during the hydrothermal treatment in alkali solutions[12]. Under the current hydrothermal conditions, like ammonium titanate, the insoluble ammonium niobate may be decomposed to form crystalline oxide at 150 °C. For other alloy elements, Sn is soluble in strong alkali solutions, Zr is not reactive to strong alkali solutions, and Mo is not corrodible by alkali solutions. No compounds of Zr, Sn and Mo are detected.

For the heat treated TLM120 sample, the peaks of anatase or niobium oxide are still not present (Fig.2). The similar nanosheet film on hydrothermally treated Ti is composed of anatase TiO_2 after the heat treatment at 400 °C[10]. The failure of detecting crystalline anatase by XRD may be due to the small thickness of the nanosheet film. The small peak at 2θ=25.2° for the TLM150 sample grows stronger after heat treatment, indicating the crystallization of TiO_2/Nb_2O_5 during the annealing process. In addition, the microstructure of TLM alloy is influenced by the heat treatment. The peaks of α-Ti are increased, revealing the decomposition of meta-stable β phase during the heat treatment. Therefore, the surface modification methods with lower processing temperatures can help minimizing the detrimental thermal effects on structure and properties of the near β type titanium alloys.

2.3 Elemental and bonding analyses

XPS spectra of Ti 2p, Nb 3d, N 1s and O 1s of the hydrothermally treated and the heat treated TLM samples are shown in Fig.3. The alloy elements of Sn, Zr and Mo are not detectable. Titanium at the sample surface presents mainly in

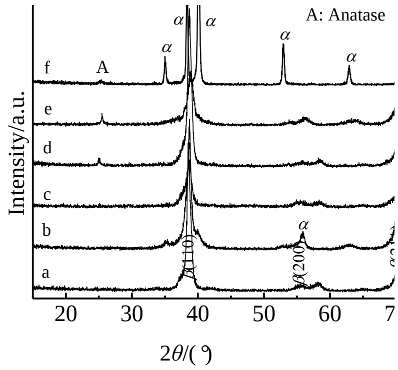


Fig.2 XRD patterns of the hydrothermally treated and the heat treated samples: (a) TLM, 120 °C; (b) TLM, 120 °C, heat treated; (c) TLM, 135 °C; (d) TLM, 150 °C; (e) TLM, 150 °C, heat treated; (f) Ti, 150 °C

the form of TiO_2/titanate, having the binding energies of 464.3 eV (Ti $2p_{1/2}$) and 458.5 eV (Ti $2p_{3/2}$). In Nb 3d spectra, the two peaks at 210.0 eV ($3d_{3/2}$) and 207.2 eV ($3d_{5/2}$) indicate that the bonding of Nb is in the form of Nb_2O_5/niobate. The TLM120 sample has lower intensities of Nb 3d peaks than the TLM150 sample, with the atomic Nb/Ti ratios of 4.1% and 25.4%, respectively. It is noted that the atomic ratio of Nb/Ti is 20.1% for the polished TLM sample. This is likely because soluble niobate salts (e.g. $K_8Nb_6O_{19}\cdot 10H_2O$) are formed at low temperatures (e.g. 120 °C), but insoluble niobate salts (e.g. $KNbO_3$) or niobium oxides are formed at 150 °C during the hydrothermal treatment in alkali solutions[12].

In the N 1s spectra, the peaks at 402.3 and 400.2 eV are assigned to N species in ammonium salts and the N-C bonding, respectively[10,13]. The peaks at 400.2 eV are obvious for the hydrothermally treated samples, but they disappear after heat treatment, indicating the removal of urea and its variants by the heat treatment. The peak at 402.3 eV is very weak for the TLM120 sample, and is vanished for the TLM150 sample after heat treatment. Therefore, the decomposition of ammonia titanate, urea and its variants occurs during the heat treatment. In addition, the N 1s peaks are much lower compared with the O 1s peaks for all samples. The atomic N/O ratio is only 3.7% for TLM120 sample after heat treatment. In the O 1s spectra, the main peak at 530.0 eV is attributed to TiO_2, and the shoulder peak at 532.1 eV is related to hydroxyl groups. The hydroxyl groups of the films will help improving hydrophilicity of the treated TLM samples.

2.4 Adhesion and hydrophilicity tests

Rockwell-C indentation test is a standardized method to evaluate the adhesion of ceramic coatings[9]. The indent morphologies of the hydrothermally and heat treated TLM samples are shown in Fig.4a, 4b. For the both samples, no cracks or delamination of the oxide films are observed around the indent circumference, revealing good adhesion quality, HF1.

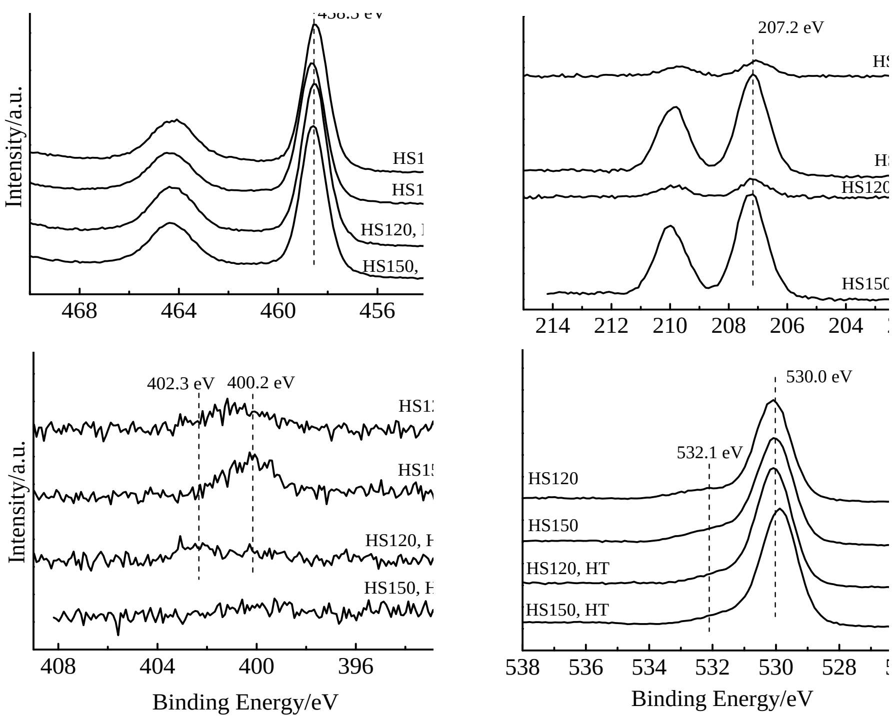


Fig.3 XPS spectra of the hydrothermally treated (HS) and the heat treated (HT) TLM alloy samples: (a) Ti 2p, (b) Nb 3d, (c) N 1s, and (d) O 1s

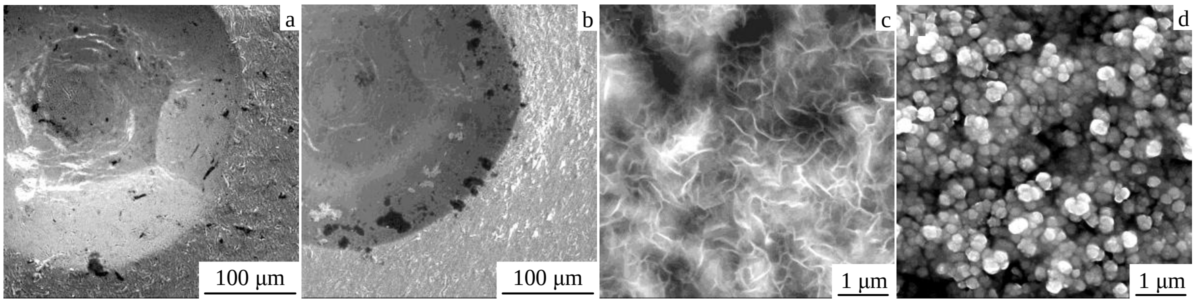


Fig.4 SEM indent morphologies of the TLM alloy samples and their surfaces tested with a home-used scotch tape: (a, c) TLM, 120 °C, heat treated; (b, d) TLM, 150 °C, heat treated

The nanosheet film of TLM120 sample is grown from the alloy substrate by a conversion reaction, and thus it is adherent and conformal to substrate deformation during the indentation. For TLM150 sample, the particles grow by gradually depositing in the nanoporous film to form a coating layer (Fig.1g, 1h). Nevertheless, the coating layer is well adherent by the indentation test. In addition, the similar indent diameters of the two samples (360 μm) reveal that the both films are too thin to influence the load bearing capacity of the samples at the test load of 300 N. The adhesion of the films is also tested with a home-used scotch tape[14]. The both films are so strong that they do not peel off, even capture the glue of the tape after detached (Fig.4c, 4d).

The hydrophilic surface is beneficial for biological properties of materials, e.g. the bioactivity and the bone- bonding behavior[15,16]. The polished TLM sample has a water contact angle around 67.6±8.2°. The hydrothermally and heat treated TLM samples are highly hydrophilic, with the contact angles below 10°. This is consistent with the reported high- or super-hydrophilicity of the nanostructured titania films consisting of nanosheets[10], nanotubes[17], etc. However, the contact angles of the heat treated TLM120 and TLM150 samples increase to 50°~70° after ageing in air for 7 d. The reduced hydrophilicity of titania films during aging is due to the replacement of absorbed hydroxyl groups by oxygen at the film surface[18]. The contact angles are returned to be below 10° after 3 h UV illumination treatment. The containing of Nb element does not influence the photo-induced hydrophilicity of the TiO_2 film. The hydrophilic surface would be good for its biocompatibility. The related biological tests will be carried out in the following work.

3 Conclusions

1) The low modulus TLM alloy can be obtained after it is subjected to hydrothermal treatments with a urea solution followed by heat treatment.

2) Nanosheet films of ammonium titanate are formed at 105 and 120 °C, while nanoparticle film of anatase TiO_2 containing Nb_2O_5 is formed at 150 °C on the alloy surface.

3) The subsequent annealing heat treatment at 400 °C decomposes the ammonium salts and crystallizes titania. The obtained oxide films have good adhesion. The duplex treatment will enhance hydrophilicity of the TLM alloy.

References

1 Yu Z T, Zhou L. *Mater Sci Eng A*[J], 2006, 438: 391
2 Fu T, Wang C P, Guo Z K. *Rare Metal Materials and Engineering*[J], 2011, 40(5): 889 (in Chinese)
3 Zhou Y, Wang Y B, Zhang E W *et al*. *Biomed Mater*[J], 2009, 4: 044 108
4 Zheng C Y, Li S J, Tao X J *et al*. *Mater Sci Eng C*[J], 2007, 27(4): 824
5 Kokubo T, Kim H M, Kawashita M *et al*. *J Mater Sci Mater Med*[J], 2004, 15: 99
6 Fawzy A S, Amer M A. *Dental Mater*[J], 2009, 25: 48
7 Fujibayashi S, Nakamura T, Nishiguchi S *et al*. *J Biomed Mater Res*[J], 2001, 56: 562
8 Ravelingien M, Mullens S, Luyten J *et al*. *Appl Surf Sci*[J], 2009, 255: 9539
9 Heinke W, Leyland A, Matthews *et al*. *Thin Solid Films*[J], 1995, 270: 431
10 Hosono E, Matsuda H, Honma I *et al*. *Langmuir*[J], 2007, 23: 7447
11 Li J M, Yu Y X, Chen Q W *et al*. *Cryst Growth Design*[J], 2010, 10: 2111
12 Zhou H M, Zheng S L, Zhang Y. *Nonferrous Metals*[J], 2004, 56(2): 61 (in Chinese)
13 Chang J C, Tsai W J, Chiu T C *et al*. *J Mater Chem*[J], 2011, 21: 4605
14 Kim H M, Miyaji F, Kokubo T *et al*. *J Mater Sci Mater Med*[J], 1997, 8: 341
15 Chun Y, Levi D S, Mohanchandra K P *et al*. *Mater Sci Eng C*[J], 2009, 29: 2436
16 Ueno T, Yamada M, Suzuki T *et al*. *Biomater*[J], 2010, 31: 1546
17 Miyauchi M, Tokudome H. *J Mater Chem*[J], 2007, 17: 2095
18 Wang R, Sakai N, Fujishima A *et al*. *J Phys Chem B*[J], 1999, 103: 2188

一种低模量 Ti-Nb 基合金的水热法表面改性

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摘　要：采用尿素溶液对一种低模量近*β*型钛合金（Ti-25Nb-3Zr-2Sn-3Mo，或 TLM 合金）进行不同温度的水热处理。采用 SEM、XRD、XPS、压入法和接触角测试分析了 TLM 合金处理后的表面结构、化学成分、附着性和亲水性。在 105 和 120 ℃水热处理后，合金表面形成了钛酸铵的纳米片薄膜；而 150 ℃水热处理后形成了纳米颗粒薄膜，由锐钛矿 TiO_2 和 Nb_2O_5 组成。随后的 400 ℃退火热处理使铵盐分解和二氧化钛结晶。生成的氧化物薄膜具有良好的附着性。复合处理增强了 TLM 合金的亲水性，这有利于改善其生物相容性。

关键词：钛合金；生物材料；水热；TiO_2；亲水性

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