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Surface modification with SiO_2 coating on biomedical TiNi shape memory alloy by sol−gel method

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Abstract: The effect of heat treatment on the transformation temperature of Ti−52.2%Ni (mole fraction) alloy was studied using differential scanning calorimetry (DSC). The transformation temperatures of the alloy can be adjusted effectively by heat treatment. Dense and stable SiO_2 coatings were deposited on the surface of the pre-oxidized TiNi alloy by sol−gel method. The bonding strength of films and matrix was (65.9±1.5) N. The electrochemical corrosion test shows that the TiNi alloy with SiO_2 coating has excellent corrosion resistance in the Hank's simulated body fluid. The release behaviors of Ni ion of the alloy with and without SiO_2 coating implanted in the acoustic vesicle of guinea pig were studied by EDS testing, which was inhibited effectively by the dense and stable SiO_2 coating on the alloy.

Key words: TiNi shape memory alloy; surface modification; SiO_2 coating; corrosion resistance; biocompatibility

1 Introduction

The TiNi-based shape memory alloys (SMAs) were preferable for most applications due to their good stability, practicability, superior thermo-mechanic performance and excellent biocompatibility [1−5]. Furthermore, their excellent shape memory property allowed them to adapt to the shape of certain organ when exposed to body temperature, making them to be widely used in balloon expandable devices, bone plate set and straddle nail, etc. The transformation temperature of the alloy was one of the key factors for its usage, and it could be adjusted by alloy composition and heat treatment [6−10]. The alloy composition was difficult to control precisely during melting and casting. However, the heat treatment could be an effective way to adjust the transformation temperature [8,9].

The release of Ni ion should be considered when the TiNi SMAs were used as implants in the human body, since the excessive Ni ion would be harmful to people's health. For medical application, the modification of the surface of TiNi SMAs was necessary to inhibit the release of Ni ion and improve the corrosion-resistance of the alloy. Various methods to fabricate coating on TiNi alloy have been reported in Refs. [11−14], and the coating on the surface of the alloy included TiO_2/NiO, ZrO_2, TiN/Ti_2N, TiO_2/TiC, Ca/P, Mo+C and so on [11].

In this work, the effect of heat treatment on phase transformation temperature was studied. A preparing process of the novel SiO_2 coating on TiNi SMAs by sol−gel method was also studied. The TiNi SMAs with and without SiO_2 coating were implanted in the acoustic vesicle of guinea pig, and their corrosion behavior, biocompatibility and the Ni ion release behaviors were also investigated.

2 Experimental

The Ti−52.2%Ni (mole fraction) SMA was first

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melted and cast using the consumable electrode vacuum furnace, and then the ingot was vacuum induction-melted 4 times. The ingot was homogenized at 800 °C for 60 min, and then hot-forged followed by hot-rolling. The samples cut from the hot-rolled sheet were solution-treated at 800 °C for 60 min followed by water-quenching, and then aged at different temperatures for different time. The transformation temperatures of the samples treated with heat-treatment were measured using a NETZSCH STA 449c thermal analyzer.

The PVA/SiO_2 sol was prepared by mixing medical polyvinyl alcohol (PVA, the degree of polymerization was 1750 and the content of sodium acetate was less than 0.5%), ethyl orthosilicate (TEOS), deionized water and medical ethanol. The sol was stirred using a homothermic magnetic stirrer during the preparation process. The process was as follows: mixing PVA with deionized water→adding a certain amount of TEOS and ethyl alcohol→adding hydrochloric acid and propanetriol to adjust the pH value of the sol. The TiNi SMA samples were heated in the atmosphere to form an oxide layer on the surface of them before coating. After fully-immersed into the PVA/SiO_2 sol for 30 s, the samples were pulled up at different pulling rates, then dried in the oven at 75 °C, and sintered under inert gas. The bonding strength of coating and matrix was measured by a WS−2005 type automatic coating adhesion scratch tester at the loading rate of 10 N/min and the maximum load of 80 N. The microstructure of the coating was observed using a Sirion 200 scanning electron microscope.

The corrosion experiment was conducted on an IM6ex electrochemical workstation in the potential range of −0.2 to −0.8 V and at the scanning rate of 2 mV/s. The corrosive medium was Hank's simulated body fluid consisting of NaCl (8.0 g), KCl (0.4 g), $CaCl_2$ (0.14 g), $NaHCO_3$ (0.35 g), $C_6H_{12}O_6$ (1.0 g), $MgCl_2·6H_2O$ (0.1 g), $MgSO_4·7H_2O$ (0.06 g), $Na_2HPO_4·2H_2O$ (0.06 g), KH_2PO_4 (0.06 g) and distilled water (1 L). The solution had a pH value of 7.4 with temperature of (37±0.5) °C.

TiNi SMAs with and without coating were implanted in the acoustic vesicle of guinea pig. The biocompatibility and the releasing behavior of Ni ion were studied using a Sirion 200 scanning electron microscope equipped with a GENESIS 60S energy dispersive spectroscope.

3 Results

3.1 Change of transformation temperature of sample during heat treatment

Figure 1 shows the variation of transformation temperature of the alloy aged at different temperatures for 30 min. The austenite transformation start temperature (A_s) and austenite transformation finish temperature (A_f) decrease obviously with the increase of aging temperature, while the martensite transformation start temperature (M_s) and martensite transformation finish temperature (M_f) increase slowly and approach the maximum value at 450 °C, and then decrease slowly with increasing the temperature. The transformation hysteresis decreases continuously with increasing the aging temperature.

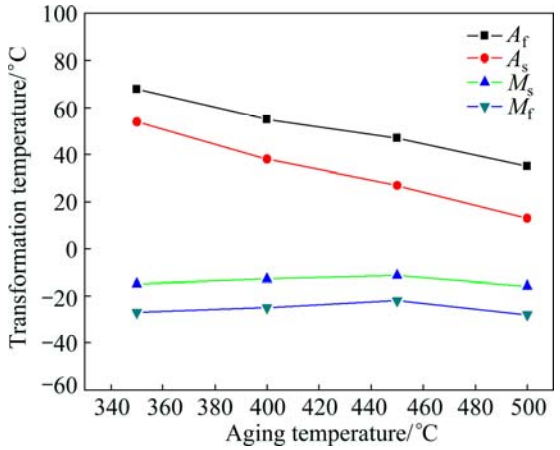

Fig. 1 Variation of transformation temperature with aging temperature

Figure 2 shows the variation of transformation temperatures of the alloy aged at 450 °C for different time. With increasing the aging time, A_s and A_f decrease, M_s and M_f increase slowly, and the transformation hysteresis decreases continuously. As the alloy was solution-treated at 800 °C and water-quenched, and then aged at 450 °C for 60 min, A_f, A_s, M_s and M_f are about 40, 23, −7 and −20 °C, respectively.

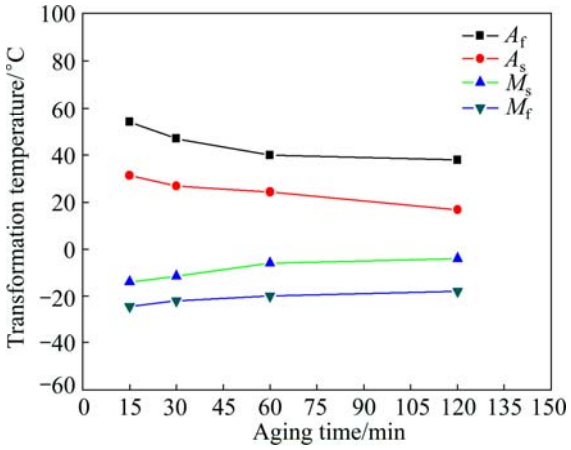

Fig. 2 Variation of transformation temperature with aging time

3.2 Microstructure of SiO_2 coating prepared by sol−gel method

Through orthogonal tests, the suitable processing parameters to produce SiO_2 coating on the tested alloy were that the mass ratio of polyvinyl alcohol (PVA) to

ethyl orthosilicate (TEOS) was 1:3, the pulling rate was 3 mm/min, and the sintering temperature was 550 °C.

The surface of some TiNi samples was pre-oxidized before coating for comparison. The typical morphologies of the prepared SiO_2 coatings are shown in Fig. 3. Figures 3(a) and (b) show the typical coatings prepared with and without pre-oxidizing process, which are uniform and dense. The cross section morphologies and EDS linear scanning results of the coatings are shown in Figs. 3(c) and (d), indicating that the contents of Ti and Ni decrease sharply from the matrix to coating, however, the density of the coating on the pre-oxidizing sample (Fig. 3(c)) is much higher than that on no pre-oxidizing sample (Fig. 3(d)). It is suggested that the TiO_2 formed on the TiNi alloy by pre-oxidized process can promote the formation of SiO_2 coating, and the diffusion of Ni ion can be effectively held by the SiO_2 coating.

Figure 4 shows the adhesion strength between the film and matrix. The cohesive strength of the SiO_2 coating on the pre-oxidized sample and no pre-oxidized sample are (65.9±1.5) and (40.85±1.75) N, respectively. The relatively high cohesive strength of SiO_2 coating on the pre-oxidized sample may be attributed to the low linear thermal expansion coefficient of the composite coating on oxidized surface (TiO_2+SiO_2 composite coating).

3.3 Corrosion behavior of specimen with and without SiO_2 coating

The specimens with and without SiO_2 coating on pre-oxidized sample were immersed into the Hank's simulated body fluid for different days, and the polarization curves of specimens were measured and are shown in Fig. 5.

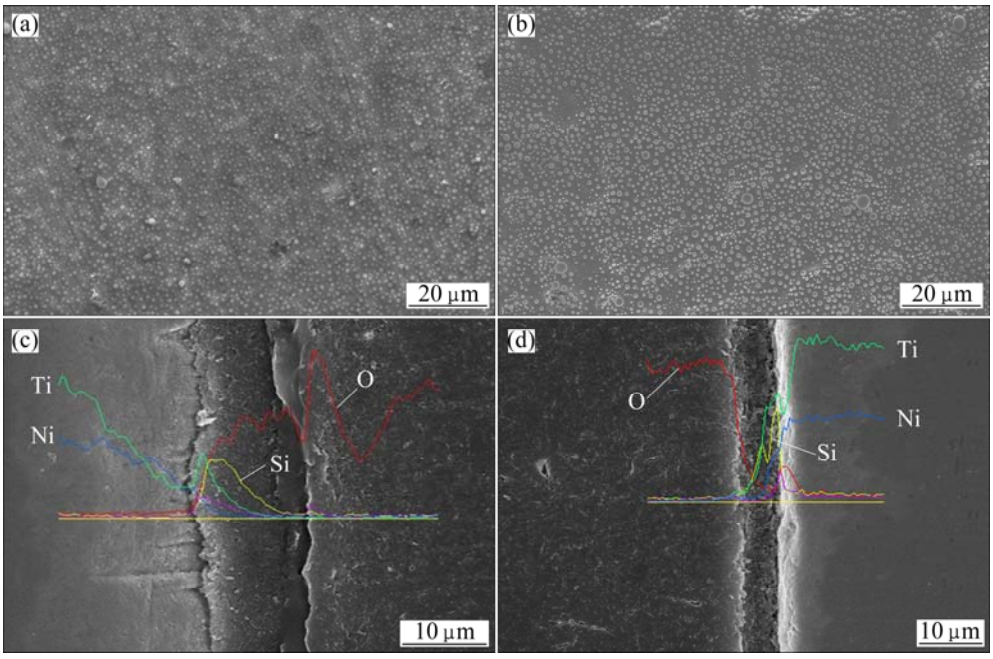

Fig. 3 Typical morphologies of SiO_2 coatings on pre-oxidizing sample (a) and no pre-oxidizing sample (b), and liner distribution of elements of coating on pre-oxidizing sample (c) and no pre-oxidizing sample (d)

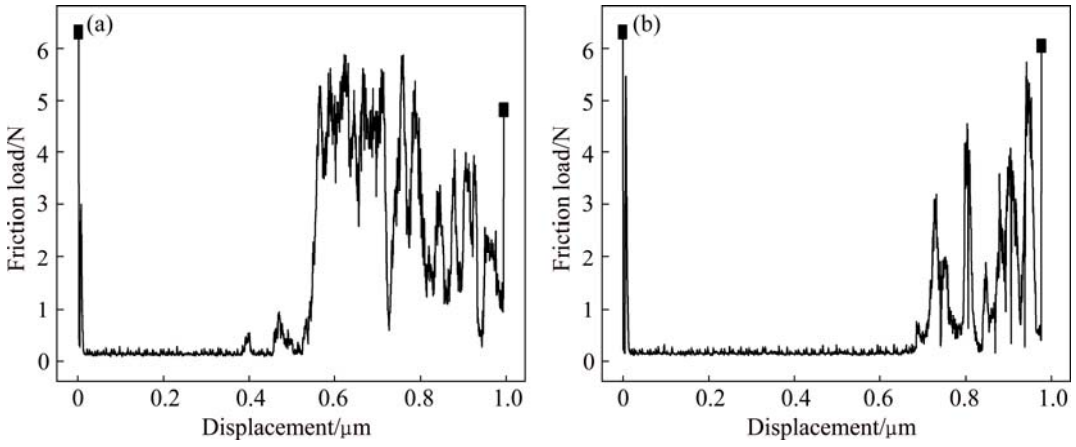

Fig. 4 Relationship between friction load and displacement of coating on pre-oxidizing sample (a) and no pre-oxidizing sample (b)

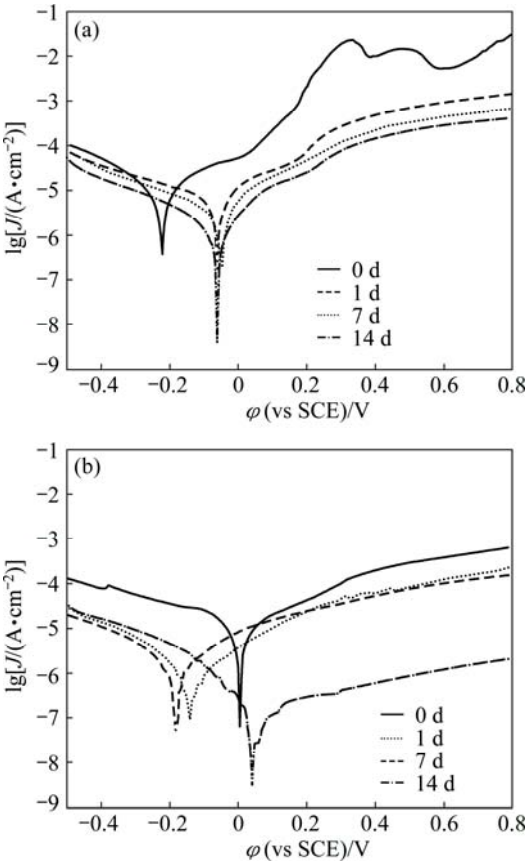

Fig. 5 Polarization curves of specimens immersed in simulated body fluid for different days without SiO_2 coating (a) and with SiO_2 coating (b)

The polarization resistance of the alloy can be calculated by

$$R_p = \frac{b_a b_c}{2.3(b_c - b_a)J_{corr}} \quad (1)$$

where b_a is the anode Tafel slope, b_c is the cathode Tafel slope, J_{corr} is the corrosion current density, φ_{corr} is the corrosion potential and R_p is the polarization resistance. Table 1 summarizes the characteristic parameters of the electrochemical test according to Fig. 5. Normally, the corrosion rate has a linear relationship with the corrosion current density. Therefore, the current density and polarization resistance can be used to evaluate the corrosion resistance property of the alloy.

From the results listed in Table 1, it is found that the polarization resistance of coated TiNi alloy is about 4 times as high as that of no-coated TiNi alloy, which illustrates that the SiO_2 coating prepared is dense and inhibits the corrosion process of the alloy in Hank's solution effectively. The polarization resistances of both coated and no-coated alloy increase with increasing the immersing time obviously. After immersed in Hank's solution for 14 d, the polarization resistance increases from 8.09 to 164.01 kΩ·cm^2 for coated alloy, and from 1.82 to 31.47 kΩ·cm^2 for no-coated alloy. It is suggested that ions in the Hank's simulated body fluid are ready to deposit on the TiNi alloy with and without coating, and the SiO_2 coating shows good biocompatibility.

3.4 Biocompatibility of sample with and without SiO_2 coating

In order to assess the biocompatibility of the sample to the hearing organ, the samples with and without SiO_2 coating were implanted in the acoustic vesicle of guinea pig. Figure 6 shows the morphological changes of the new formed tissues on the surface of the samples with and without SiO_2 coating. Figures. 6(a) and (b) show the typical morphologies of new proliferated tissues on the implanted samples without SiO_2 coating for 56 and 112 d post-implantation, respectively, and Figs. 6(c) and (d) show those on the implanted samples with SiO_2 coating for 56 and 112 d post-implantation, respectively. For the same post-implantation period, the typical morphologies of new proliferated tissues on the implanted samples with and without SiO_2 coating are almost the same. The proliferated bone tissues are net-like on the samples for 56 d post-implantation, and sense plate-like for 112 d post-implantation. Both the SiO_2 coating and the TiNi alloy show good biocompatibility.

Figure 7 shows the morphologies and compositions of new proliferated tissues formed on the surface of implanted samples without (Figs. 7(a) and (b)) and with

Table 1 Characteristic parameters obtained from polarization curves of samples

Sample	Exposure time/d	φ_{corr}/mV	J_{corr}/(μA·cm^{-2})	b_a/(mV·dec^{-1})	b_c/(mV·dec^{-1})	R_p/(kΩ·cm^2)
Not coated	0	−223.8	16	198	−331	1.824618
	1	−61.5	6.06	89	−434	5.298801
	7	−50.5	3.02	192	−305	16.96328
	14	−52.66	1.15	128	−238	31.4688
Coated	0	3.125	10.2	304	−217	8.095351
	1	−144.1	0.993	57.8	−149.4	18.24785
	7	−185.7	1.26	147	−216	30.18326
	14	60.13	0.128	487	−53.6	164.0136

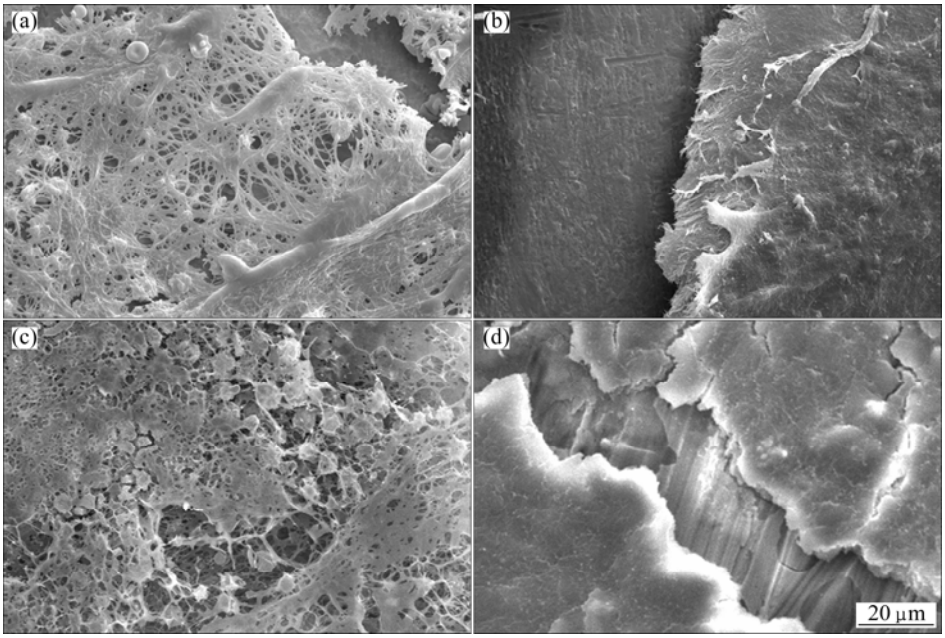

Fig. 6 Typical morphologies of new proliferated tissues formed on implanted samples without SiO_2 coating for 56 d post-implantation (a) and 112 d post-implantation (b), and with SiO_2 coating for 56 d post-implantation (c) and 112 d post-implantation (d)

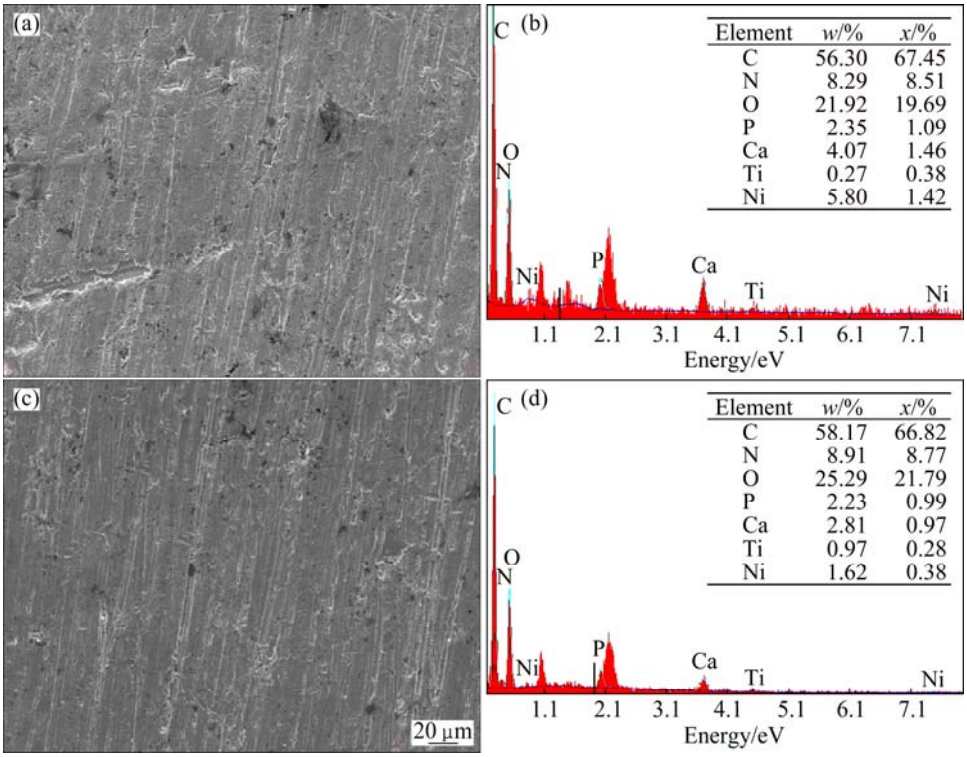

Fig. 7 Morphologies (a, c) and compositions (b, d) of new proliferated tissues formed on surface of TiNi without (a, b) and with (c, d) coating as implanted in acoustic vesicle of guinea pig for 112 d

(Figs. 7(c) and (d)) SiO_2 coating for 112 d post-implantation. The elements, including C, N, O, P, Ca, Ti and Ni, are found in both samples. Comparing two sets of data, the Ni content in the tissues formed on the surface of coated sample (0.38%) is much lower than that on the surface of no-coated sample (1.42%), which may be attributed to the inhibition of Ni release by SiO_2 coating, and a small amount of Ni detected in the coating sample may be from the substrate material of NiTi alloy because SiO_2 coating is thin. The SiO_2 coating effectively prevents the diffusion of Ni and can inhibit the release of Ni ions to human body.

4 Conclusions

1) The transformation temperatures of the tested TiNi alloy were adjusted by heat treatment. As the alloy was solid-solution treated at 800 °C, followed by 450 °C aging for 60 min, the transformation temperatures of A_s, A_f, M_s and M_f are about 40, 23, −7 and −20 °C, respectively.

2) The SiO_2 coatings were deposited on the alloy by sol−gel method. When the mass ratio of polyvinyl alcohol (PVA) to ethyl orthosilicate (TEOS) was 1:3, the pulling rate was 3 mm/min, and the sintering temperature was 550 °C, the dense and stable SiO_2 coating was prepared on the pre-oxidized TiNi alloy, and the bonding strength of films and matrix was (65.9±1.5) N. The SiO_2 film coating on the surface of TiNi SMAs can effectively reduce the release of Ni ion to the human body.

3) The TiNi alloy with SiO_2 coating has excellent corrosion resistance in corrosion experiment of Hank's simulated body fluid and good biocompatibility by implantation in the acoustic vesicle of guinea pig.

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生物医用 TiNi 记忆合金的溶胶−凝胶法 SiO_2 涂层表面改性

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摘 要：采用差示扫描量热分析法(DSC)研究热处理对 Ti−52.2%Ni(摩尔分数)合金相变温度的影响。通过热处理手段可有效调整合金的相变温度。采用优化的溶胶−凝胶工艺在预氧化的 TiNi 合金表面制备一层致密、稳定的 SiO_2 涂层，膜基结合强度为(65.9±1.5) N。电化学试验结果表明：经表面 SiO_2 涂层改性处理的 TiNi 合金在模拟体液中具有优异的耐蚀性能。经表面 SiO_2 涂层改性处理和无表面改性 TiNi 合金样品分别植入豚鼠听泡，通过扫描电镜观察和能谱分析发现 TiNi 合金表面致密稳定的 SiO_2 涂层能有效阻止镍离子从合金基质中溶出。

关键词：钛镍形状记忆合金；表面改性；SiO_2 涂层；腐蚀性能；生物相容性

(Edited by Mu-lan QIN)