OXIDE FILM ON EQUIATOMIC TiNi SHAPE MEMORY ALLOY①

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ABSTRACT By means of scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy, the oxide layers on equiatomic TiNi shape memory alloy oxidized in the temperature range from room temperature to 800 ℃ were studied. The results showed that the thin oxide film naturally formed at room temperature contains Ti element in TiO_2 state and part of Ni element in Ni_2O_3 state, leaving other Ni still in metallic state; The thin oxide films formed at 300～500 ℃ are characterized by enriched Ti and depleted Ni, both in completely oxidized state. Thick scaling layers were formed above 700 ℃, which are proved to be composed of an outer TiO_2 layer dissolved by small amount of Ni and an inner pure Ni_3Ti layer.

Key words TiNi shape memory alloy oxidation surface modification

1 INTRODUCTION

Equiatomic TiNi shape memory alloy (SMA) is a novel and promising biomaterial due to its unique and excellent shape memory effect and superelasticity. In addition to the successful application of superelastic TiNi archwire in orthodontics, various medical implants such as blood vessel stent in interventional treatment, which require long term implantation and thus higher biocompatibility, have been proposed and widely studied worldwide. The progress in practical applications of TiNi SMAs has led to extensive researches on relevant properties such as wear resistance and its improvement[1] and corrosion resistance[2]. It has been demonstrated from the results of corrosion resistance investigation that TiNi SMAs possess poorer pitting resistance than 316L stainless steel in physiological saline solution. As a result, several surface modification methods, including N^+ implantation[3], deposition of plasma polymerized tetrafluoroethylene(PPTFE)[4] and chemical passivation in acid solution[5], have so far been studied on the aim to improve its corrosion resistance and biocompatibility. We have shown in previous papers[6, 7] that thermal oxidation can substantially improve the corrosion resistance and biocompatibility of TiNi SMAs. The present research was conducted to clarify the oxidation course and oxide film structure at an extended range of oxidation temperature in an effort to further the understanding of positive effect of oxidation.

2 MATERIALS AND EXPERIMENTS

The alloy used in the experiments is a binary TiNi with a chemical composition (in mole fraction) of Ti-50% Ni and a reverse transformation temperature A_s of about 31 ℃. Specimens with a dimension of 15 mm × 15 mm × 0.7 mm were mechanically ground with wet emery paper up to 800 mesh and then polished with diamond paste up to 1 μm before oxidation. The oxidation was conducted inside an electrical furnace in air. A Shimazu LIBROR L200SM electronic balance was used to measure the weight variation, with an accuracy of 10^{-5} g. The scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were performed on a Hitachi S570 scanning electron microscope. The crystal structure of the scaling layers were analyzed on a

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D/max-B type X-ray diffraction meter using CuK_α radiation. X-ray Photoelectron Spectroscopy (XPS) was conducted on an ESCALABMK II type X-ray photoelectron spectroscope.

3 RESULTS AND DISCUSSION

3.1 Scaling layers formed at high temperature

Fig. 1 shows the oxidation kinetic curves at various temperature. It can be seen that the oxidation at 700 and 800 ℃ may be described by a parabolic rate law, while at 500 and 600 ℃ the logarithmic rate law may represent the oxidation course. This is in consistence with the results reported in Ref. [8].

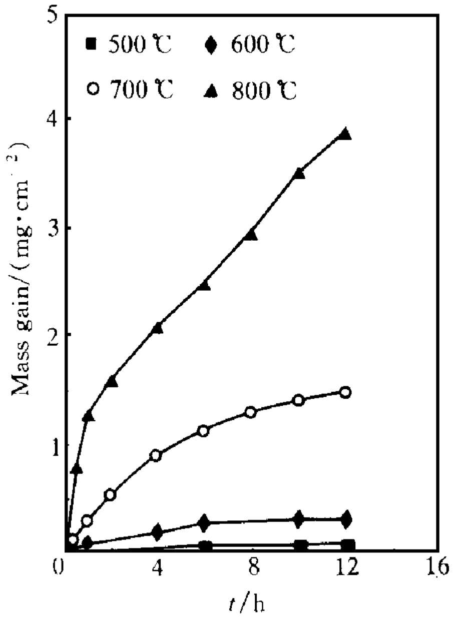

Fig. 1 The oxidation kinetic curves of TiNi SMA specimens at various oxidation temperatures

The microstructure of the scaling layer on the specimen oxidized at 800 ℃ for 6 h is shown in Fig. 2. It is clearly seen that the scaling layers are composed of two layers. By means of EDX, the Ti/Ni ratio in the outer and inner layer was determined to be 1∶0.19 and 1∶2.97 (atomic ratio), respectively. And the Ti∶Ni ratio in the TiNi matrix was also confirmed concurrently to be 1∶0.98, suggesting that the accuracy is pretty good. In order to identify the crystal structure of the scaling layers, the X-ray diffraction test was employed and the results are shown in Fig. 3. Fig. 3(a) is the spectrum from the outer layer, which can be identified to be rutile TiO_2 structure. The experiments revealed that this rutile TiO_2 layer was loosely attached on the inner layer at room temperature and thus was able to be cleared easily. As a result, the spectrum from the inner layer was obtained and is shown in Fig. 3(b), which can be identified to be the hexagonal Ni_3Ti.

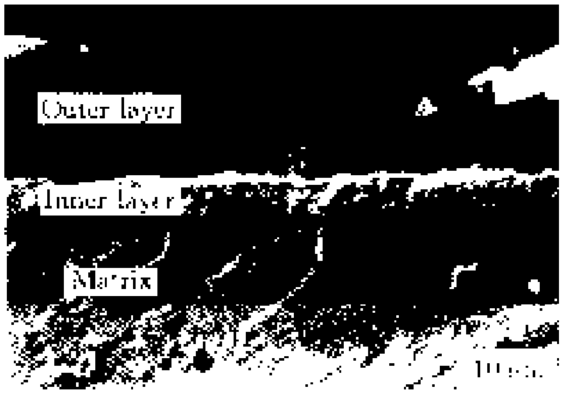

Fig. 2 The SEM micrograph of scaling layers on TiNi specimen oxidized at 800 ℃ for 6 h

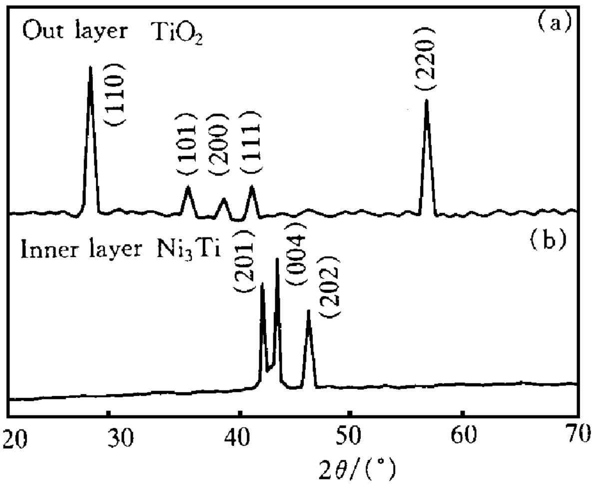

Fig. 3 The X-ray diffraction spectra from scaling layers on TiNi specimen oxidized at 800 ℃ for 6 h

Based on the above results of X-ray diffraction and EDX, it can be concluded that the scaling layers on the specimen oxidized at 800 ℃ for 6 h are composed of an outer TiO_2 layer containing small amount of Ni and an inner Ni_3Ti layer. This form of scaling layers is resulted from the selective oxidation of TiNi SMA owing to significant difference in affinity of Ti and Ni element with O element. Selective oxidation makes Ti element preferentially oxidized during oxidation process, which drives the Ni ions to diffuse from oxide film towards interior matrix or/and Ti ions to diffuse in opposite direction. As a result, the outer oxide layer becomes Ti enriched while the region of the matrix close to the oxide layer becomes Ni enriched. As the Ni concentration in this region exceeds the solubility, the Ni riched phase of Ni_3Ti, according to Ti-Ni phase diagram[8], must precipitate and grow.

In practical processing of TiNi SMAs, the oxide layers are frequently washed in mixed solution of HNO_3, HF and H_2O. Since the intermetallic compound Ni_3Ti is considerably more resistant to the attack of HF acid than TiNi matrix, it will be difficult for TiNi SMAs to obtain good surface quality after washing in HNO_3 and HF acid solution when the Ni_3Ti layer is thick and compact. On the other hand, both Ni_3Ti and TiNi show the metallic lustre and are therefore difficult to distinguish between them. It is extremely important that, for the medical implant made of TiNi SMAs, special care should be taken to assure that Ni_3Ti layer being completely cleared off, in order to avoid the highly cytotoxic Ni_3Ti from contact with living tissue.

3.2 Thin oxide films formed at lower temperature

When the oxidation is conducted below 500 ℃ the oxide film is thinner and is only able to be analyzed by XPS and auger electron spectroscopy. Fig. 4 shows the high resolution XPS spectra of Ni2*p*, Ti2*p* and O1s from three different surface states. For the specimen naturally oxidized at room temperature (curves b), the Ni$2p_{3/2}$ spectrum is composed of two peaks with binding energy of 856.3eV and 853.1eV, which correspond to Ni_2O_3 and metallic Ni respectively. The peaks of 530.6eV and 533.0eV in O1*s* spectrum are related to TiO_2 (or Ni_2O_3) and H_2O respectively. The Ti$2p_{3/2}$ spectrum revealed that most of the Ti is in TiO_2 state (binding energy 459.2eV), with only small quantity existing in metallic state (binding energy 455.7eV). After oxidation at 400 ℃ (curves a), it can been seen that the 853.1eV peak of Ni$2p_{3/2}$ and 455.7eV peak of Ti$2p_{3/2}$ from metallic Ni and Ti, respectively, vanish and the 533.0eV peak of O1*s* from H_2O is considerably reduced. If the naturally oxidized specimen was sputtered by Ar^+ ion

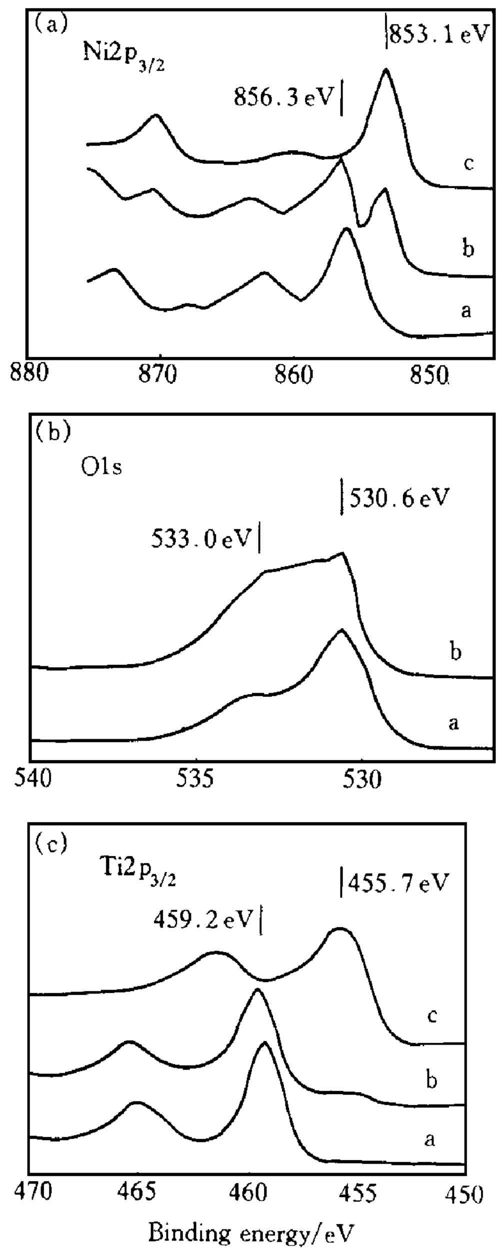

Fig. 4 The high resolution XPS spectra of Ni2*p*, O1*s* and Ti2*p* for TiNi alloy in the surface state

(a) —Oxidized at 400 ℃ 1 h;
(b) —Naturally oxidized at room temperature;
(c) —State (b) plus Ar^+ ions sputtering for 0.5 h

for 0.5h, only one peak appears in both Ni2$p_{3/2}$ and Ti2$p_{3/2}$ spectrum with binding energy of 853.1eV and 455.7eV, respectively. This further confirms that the above two peaks are related to the bulk TiNi intermetallic compound. The experiments also revealed that the Ni2p, Ti2p and O1s spectra from the specimens oxidized at 300 ℃ and 500 ℃ for 1 h take the same form as those from the specimen oxidized at 400 ℃. Their difference consists in the Ni/Ti ratio which was determined by quantitative XPS analysis, as seen in Table 1. It can be seen that the Ni/Ti ratio is decreased from 0.9∶1 to 0.27∶1 as oxidation temperature is increased from 300 ℃ to 500 ℃.

Table 1 The Ni/Ti ratio in oxide film formed at different temperatures for 1 h

Surface state	Ni∶Ti∶O atomic ratio
Naturally oxidized in air	1∶1
300 ℃ oxidation	0.9∶1∶5.5
400 ℃ oxidation	0.3∶1∶5
500 ℃ oxidation	0.27∶1∶4.5

The above results mean that for TiNi alloy specimens, thermal oxidation between 300~500 ℃ can effectively modify the existing state of Ni component in the surface oxide film, and furthermore, make Ti component considerably enriched in the surface film, which is apparently due to the selective oxidation of the alloy. Ni is generally considered as a cytotoxic metal element. This Ti-enriched thin surface film can effectively retard the Ni ion release in saline solution and considerably improve the biocompatibility of the TiNi SMAs[6, 7]. Since the oxide film formed at the temperature range from 300~500 ℃ is rather thin and thus shape memory effect and shape recovery temperature are seldom influenced by its presence[9], this low temperature oxidation is really a simple and effective surface modification method for clinical TiNi SMAs with respect to the improvement of biocompatibiliy.

4 CONCLUSION

For equiatomic TiNi SMA, the thin oxide film naturally formed at room temperature consists of completely oxidized Ti element in TiO_2 state and partially oxidized Ni element in Ni_2O_3 state, leaving other Ni in the metallic state; after oxidation at temperature above 700 ℃, thicker scaling layers which are composed of an outer TiO_2 layer dissolved by small amount of Ni and an inner pure Ni_3Ti layer, are formed. The oxidation at temperature between 300~500 ℃ produces thinner oxide films where Ti is enriched and Ni depleted, both in completely oxidized state.

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