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Surface properties of nitrogen-ion-implanted TiNi shape memory alloy

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Abstract: X-ray diffraction (XRD), auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS) were used to characterize the surface properties of the N^+-ion-implanted TiNi alloy. There is a high nitrogen content region at the outermost surface of the N^+-ion-implanted TiNi alloy. The detected nitrogen exists mainly in the form of TiN. Small amounts of Ti_3O_5 and TiO_2 also exist on the surface of the N^+-ion-implanted TiNi sample. The modified layer of the N^+-ion-implanted sample can work as an obstacle layer of the nickel's dissolution, which obstructs Ni dissolving from the TiNi surface effectively.

Key words: shape memory alloys; TiNi; surface properties

1. Introduction

TiNi shape memory alloys (SMA) exhibit a good shape memory property, super elasticity, excellent stability, and are used for surgical implantation. However, the alloy contains Ni, which is toxic and frequently causes hypersensitive reactions [1-4]. Ni dissolves into biological solution over time. Some surface modification is needed to improve the TiNi alloy's biocompatibility, such as plasma spraying, different modes of sputtering, pulse laser deposition, and so on [5]. There exist problems that relate to the adhesion of the coating. The coated surface peels off during use. Ion implantation surface treatment can obtain some modified layers without a sharp interface with the substrate materials, which avoids the problem of adhesion [6-11]. The implanted dose, implanted current, and the implanted depth can be controlled at the same time. Implantation will not change the shape and the size of the biomaterials being implanted. N-ion implantation surface treatment is used extensively to improve the mechanical properties of implanted materials [12-13]. Some of the research results have been used in biomaterial production already, but little concerns the surface modification of TiNi alloys.

2. Experiment

All the TiNi alloy substrate samples used in the experiments have a composition close to the equi-atomic ratio, namely, Ti49.8at%-Ni50.2at% alloy. The implantation of N^+ ions was carried out at a vacuum of about 2.7×10^{-4} Pa, with an acceleration voltage of 50 keV and an implanted dose of 1×10^{16} ions/cm^2. This was followed by surface analysis with X-ray diffraction (XRD), auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS).

A RINT 2200H XRD apparatus was used to detect the phase of the sample surface. The AES results were obtained using JAMP-7810 auger electron spectroscopy with a tilting angle of 30°. XPS was performed using a JPS-9010MC photoelectron spectrometer. All spectra were obtained with Mg K_α radiation. In wide scan experiments, the accelerating voltage was 8 kV and the anode current was 8 mA. The depth analysis was carried out at the voltage of 10 kV and at the current of 10 mA.

3. Results and discussion

3.1. XRD results and discussion

Fig. 1 shows the XRD results of the N^+-ion-implanted TiNi alloy. It is difficult to separate the peaks of TiNi and nitrides. For an N^+-ion-implanted TiNi alloy sample, the possibility of forming other compounds is high, but other titanium compounds or nickel compounds cannot be detected using the conventional diffractometer method. The detailed existing phases require additional analysis. To get more detailed information about the phase formation and the chemical state of the implanted sample, AES and XPS investigations were performed.

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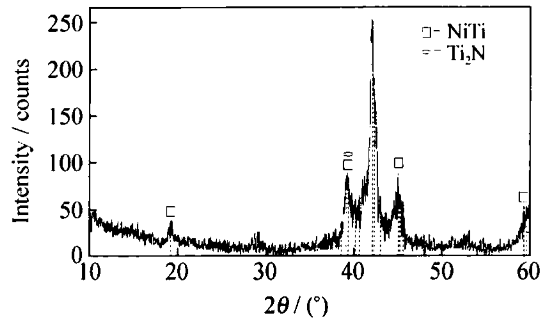

Fig. 1. XRD profile of the TiNi alloy implanted with nitrogen at the dose of 1×10^{16} ions/cm^2.

3.2. AES results and discussion

Figs. 2-3 are the AES wide scan results of the N$^+$-ion-implanted TiNi alloy. The result reveal that N, O, C, Ti, Ni peaks exist at the outermost of the surface. N really exists on the surface but N peaks and Ti peaks are difficult to separate in principle.

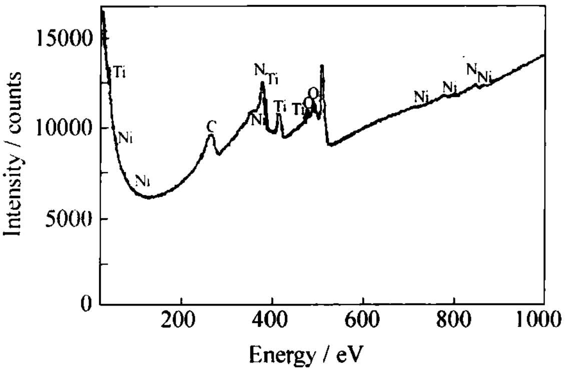

Fig. 2. AES profile of the TiNi alloy implanted with nitrogen at the dose of 1×10^{16} ions/cm^2

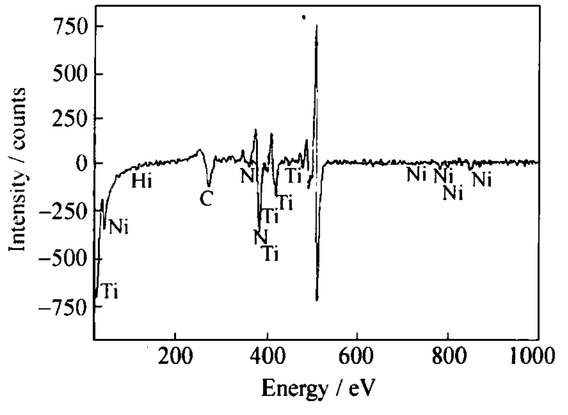

Fig. 3. AES profile (derivative) of the TiNi alloy implanted with nitrogen at the dose of 1×10^{16} ions/cm^2

3.3. XPS results and discussion

Fig. 4 is the XPS wide scan profile of the N$^+$-ion-implanted TiNi alloy. The results show that N, O, Ti, Ni, and C elements exist on the surface of the TiNi sample; the results agree well with the AES results from Figs. 2-3. The surface-modified layer of the N-ion-implanted TiNi alloy was also subjected to argon ion sputtering to obtain the depth profile of each element.

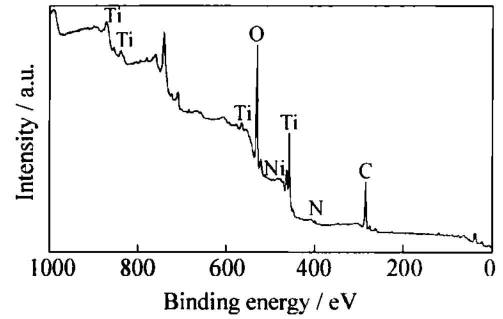

Fig. 4. XPS wide scan profile of the TiNi alloy implanted with nitrogen at the dose of 1×10^{16} ions/cm^2.

Fig. 5. shows the XPS spectra of N1s, O1s, Ti2p, Ni2p, and C1s obtained from the surface to the inside of the N$^+$-ion-implanted TiNi alloy sample. All the spectra are a function of argon ion sputtering time, and correspond to different depth regions. The total sputter time was about 350 s.

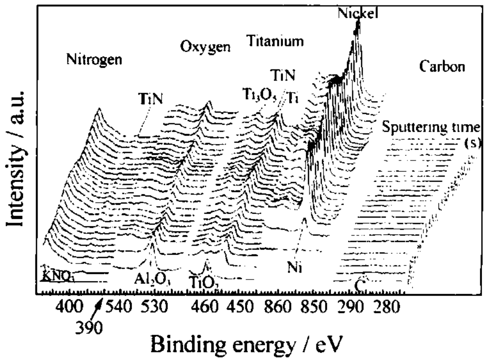

Fig. 5. N1s, O1s, Ti2p, Ni2p, C1s spectra of TiNi alloy implanted with nitrogen ions at the dose of 1×10^{16} ions/cm^2.

The N1s spectra results in Fig. 5 show that the information of nitrogen is weak on the outmost surface of the N$^+$-ion-implanted TiNi sample. A weak peak appears at the low binding energy side after 10 s sputtering, which locates at the standard binding energy of N1s in TiN (396.9 eV). There also appears another N1s peak corresponding to KNO$_3$, and the reason why KNO$_3$ exists needs more analysis.

The O1s spectra results in Fig. 5 show that the main peak of O1s is near the standard binding energy of O1s in Al$_2$O$_3$, which contributes to the Al$_2$O$_3$ base used in the experiment.

The Ti2p spectra in Fig. 5 shows that the main peak of Ti2p is at 458.7 eV on the outermost surface of the N$^+$-ion-implanted TiNi alloy sample, which corresponds to the standard binding energy of Ti2p in TiO$_2$, and indicates that the surface of the N$^+$-ion-implanted TiNi alloy is oxidized. Other two Ti2p peaks appear after 10 s of sputtering, which corresponds to the standard binding energy of Ti2p in Ti$_3$O$_5$ and titanium. The Ti2p peak contributing to TiO$_2$ disappears when the sputter time is increased. At the lower binding energy