Bioactive NiTi shape memory alloy fabricated by oxidizing in H_2O_2 solution and subsequent NaOH treatment

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Bioactive titanium metals can be prepared by alkaline treatment with NaOH solution [1–3] or oxidizing treatment with hydrogen peroxide (H_2O_2) solution [4, 5]. The former treatment produces a sodium titanate layer on titanium surface, while the latter forms a titania gel layer. Both sodium titanate layer and titania gel layer have the ability to induce deposition of bone-like apatite *in vitro* and *in vivo* and thus are considered bioactive [1–5].

Alkaline treatment is also suggested to be effective for inducing bioactivity of tantalum metal [6]. However, it is not effective for all metallic biomaterials, e.g., SUS316L stainless steel and Co-Cr-Mo alloy [2]. Chen *et al*. [7, 8] reported that bioactive NiTi shape memory alloy (SMA) could also be obtained by NaOH treatment. Owing to its unique shape memory effect and superelastic properties, NiTi SMA has been frequently used in medicine, such as orthopedic implants, stents, etc. [9–12]. However, it contains a large amount of Ni (about 50 at%), which can lead to the allergic and toxic responses [13, 14]. Therefore, the bioactivity induced by chemical treatment can enable NiTi implants to be used in medicine more safely and widely.

In this study, a bioactive NiTi SMA with wormlike surface structure was fabricated using a composite treatment by oxidizing in H_2O_2 solution and subsequent NaOH treatment, whose bioactivity was investigated by the biomimetic growth of apatite on its surface after it was soaked in simulated body fluid (SBF) for a period of time.

A commercially available NiTi (50.8 at% Ni) SMA plate for medical applications with a martensite start temperature (M_s) of −12.8 °C and an austenite finish temperature (A_f) of 33.4 °C (Beijing Gee SMA Technology Co. Ltd, China) was cut into small rectangular blocks (10 × 10 × 1 mm^3). All samples were cleaned separately in acetone, ethanol, and deionized water for 10 min, and then chemically polished to remove the native surface oxides for 10 min in Kroll's reagent: a mixture of 2 ml hydrofluoric acid (HF, 40%), 4 ml nitric acid (HNO_3, 40%), and 994 ml deionized water. The samples were subsequently ultrasonically washed in acetone for 10 min and in deionized water for 10 min. They were divided into two groups. The first group was used as control (denoted as the chemically-polished NiTi substrate). The second group was firstly oxidized in a boiling aqueous solution containing 30% H_2O_2 for 2 hr and ultrasonically rinsed again with deionized water for 10 min, and then treated in 1 M NaOH aqueous solution at 60 °C for 24 hr and ultrasonically rinsed again with deionized water for 10 min (denoted as the pretreated NiTi SMA).

After being ultrasonically washed in acetone and rinsed again in deionized water, the pretreated NiTi SMA and the chemically-polished NiTi substrate were soaked in a simulated body fluid (SBF) for 12 hr and 24 hr. The SBF solution was not replenished during the soaking procedure. The SBF solution was buffered at pH 7.4 with trimethanol aminomethane-HCl. The ionic concentrations in the SBF solution are nearly equal to those in human body blood plasma and are (mM): Na^+ 142.0, K^+ 5.0, Ca^{2+} 2.5, Mg^{2+} 1.5, HCO_3^- 4.2, Cl^- 148.5, HPO_4^{2-} 1.0, and SO_4^{2-} 0.5 15].

The XRD patterns were taken with an X-ray diffractometer (RAD IIA, Rigaku, Japan) operated with Cu Kα under 40 kV and 25 mA, equipped with a thin-film attachment on which the glancing angle was 1°. Samples were XPS analyzed using a VG Scientific ESCALAB 5 spectrometer with monochromatic Al Kα (1486.6 eV) X-ray radiation. The operating vacuum conditions in the chamber were better than 10^{-8} mbar. High resolution XPS spectra over the Ti 2p, Ni 2p, O 1s and Na 1s ranges were recorded for each sample at 20 eV pass energy, and then were used for quantification. The C 1s peak was used to standardize the spectra for any charging effects. The composition of the surface was calculated from the peak areas after subtraction of a Shirley background with reference to the

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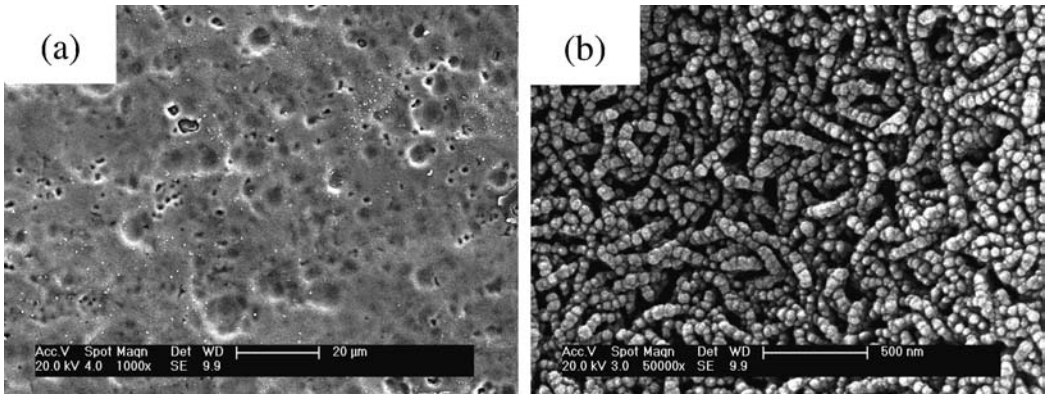

Figure 1 SEM images of the surface of NiTi SMA after having oxidized in a boiling 30% H_2O_2 solution and subsequently treated in 1 M NaOH solution.

relevant atomic sensitivity factors [16]. The experiments were repeated with at least three different samples. Data analyses and quantification were carried out by the software provided by the manufacturer. The surface morphology of the samples was observed by a Philips XL30 FEG SEM after the surfaces were coated with gold films.

Some submicron pores and grain boundaries were observed on the surface of the chemically-polished NiTi SMA (not shown here), which may be due to the treatment with Kroll's reagent. The XPS element analysis indicates the surface concentration of oxygen on the chemically-polished NiTi sample is only about 7.9 at%. Obviously the native surface oxides on NiTi SMA have been removed successfully by chemical polishing treatment. After the chemically-polished NiTi SMA oxidized in H_2O_2 solution, the surface concentration of oxygen increases to 58.4 at%, while that of Ni decrease sharply from 47.5 to 6.7 at%. The results suggest that a Ti oxide layer was formed on NiTi substrates due to H_2O_2 treatment, which is in favor of good biocompatibility of NiTi SMA for medical applications.

Fig. 1 shows SEM images of the surface of NiTi SMA after having oxidized in a boiling 30% H_2O_2 solution and subsequently treated in 1 M NaOH solution. It can be found that the composite treatment by oxidizing in H_2O_2 solution and subsequent NaOH treatment results in the formation of the wormlike surface structure on NiTi substrate. The XPS element analysis shows that the chemical composition of this wormlike surface layer on NiTi substrate was (at%): Ti 32.64, Ni 5.66, O 58.52, and Na 3.18. It is obvious that the presence of Na element can be attributed to the subsequent NaOH treatment after H_2O_2 treatment.

Fig. 2 shows the characteristic parts of XRD patterns of the surface of NiTi SMA after having oxidized in a boiling 30% H_2O_2 solution and subsequently treated in 1 M NaOH solution in comparison with the chemically-polished NiTi substrate. It can be seen that for the sample after the composite pretreatment by H_2O_2 and NaOH solutions, sodium titanate (Na_2TiO_3) and rutile TiO_2 phase were also present besides the intermetallic NiTi substrate phase. Therefore, the wormlike surface layer on the pre-

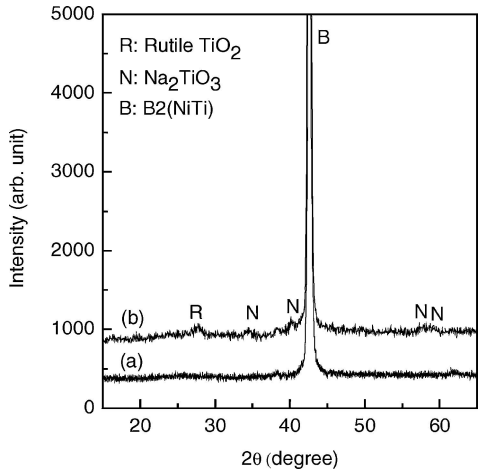

Figure 2 XRD spectra of the surfaces of NiTi SMAs: (a) after chemical polishing; (b) after oxidizing in boiling 30% H_2O_2 solution and subsequently treating in 1 M NaOH solution.

treated NiTi SMA is mainly comprised of sodium titanate and TiO_2 phases. And its crystallinity is relatively low as indicated by the broadening XRD peaks with low intensities in Fig. 2.

Fig. 3 depicts the surface views of the pretreated NiTi SMA after soaking in a simulated body fluid for 12 and 24 hr. After 12 hr immersion in the simulated body fluid, some single and clustered ball-like particles are observed on the surface of the pretreated NiTi SMA (Fig. 3a). After an immersion time of 24 hr, both the number and the size of these ball-like particles increase. In contrast, no new substance could be found on the surface of the chemically-polished NiTi substrate even after soaking in SBF for 24 hr (not shown here). The XRD patterns obtained from the surface of the pretreated NiTi SMA after immersion in SBF for 24 hr are shown in Fig. 4. The peaks of crystalline apatite can be easily identified in the XRD spectra indicating the formation of a new surface layer composed of crystalline apatite. The broadening of the peaks suggests that the apatite particles formed on the pretreated NiTi SMA are superfine or have low crystallinity.

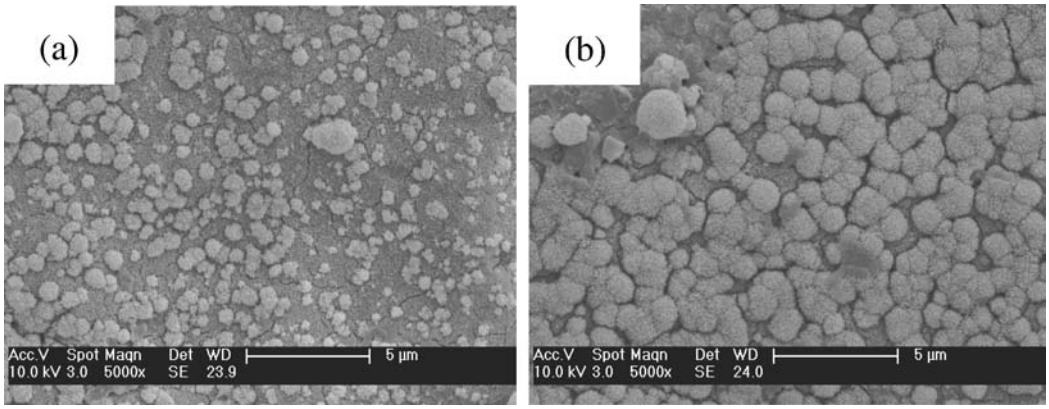

Figure 3 SEM images of the apatite deposited on bioactive NiTi SMA in SBF after different immersion times: (a) 12 hr, (b) 24 hr.

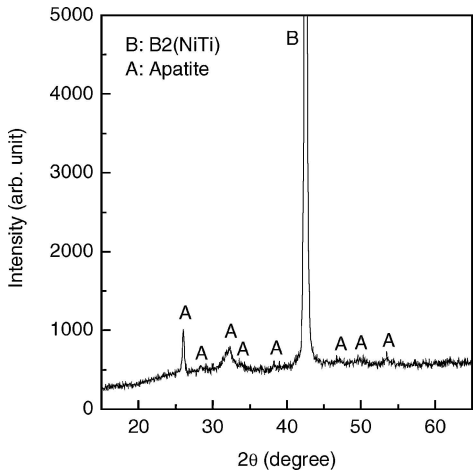

Figure 4 XRD spectra of the apatite deposited on bioactive NiTi SMA in SBF after 24 hr.

The results from XPS, SEM, and XRD reveal that a Ti oxide layer was firstly formed on the surface of NiTi substrate after having oxidized in H_2O_2 solution, and then a sodium titanate/TiO_2 layer with wormlike surface structure was formed *in situ* on the pretreated NiTi SMA by the reaction of Ti oxide with NaOH solution. The results of the SBF soaking test confirm that apatite cannot form on the surface of the chemically-polished NiTi substrate after soaking in SBF for 24 hr, but on the other hand, bone-like apatite can form on the surface of the pretreated NiTi SMA after soaking in SBF for a shorter time, indicating the bioactivity of NiTi SMA for medical applications can be improved by oxidizing in H_2O_2 solution and subsequent NaOH treatment. It is well known that the surface plays an important role in the response of the biological environment of the artificial biomedical device. Therefore, it is logical to believe that the improvement of the bioactivity of NiTi SMA results from the modified surface by the formation of the sodium titanate/TiO_2 surface layer.

As we know, TiO_2 has better biocompatibility than Ti [17], and a surface layer of TiO_2 can restrict a potential nickel release from NiTi substrate [18], while sodium titanate can induce the bioactivity for the NaOH-treated titanium [1–3]. The poorly-crystallized sodium titanate in the sodium titanate/TiO_2 layer on the pretreated NiTi SMA will release Na^+ ions *via* an exchange with H_3O^+ ions in SBF. Thus many Ti-OH groups are formed on their surfaces, and the ionic activity product of the apatite in the surrounding fluid is increased by the increase of OH^{Σ} ion concentration. Ti-OH groups can induce apatite nucleation, while the increased ionic activity product accelerates apatite nucleation.

In conclusion, a bioactive NiTi SMA with the wormlike surface structure was fabricated using a composite pretreatment by oxidizing in a boiling 30% H_2O_2 solution and subsequent treatment in 1 M NaOH solution. The wormlike surface layer on the pretreated NiTi SMA is mainly composed of sodium titanate(Na_2TiO_3) and rutile TiO_2 and can induce the nucleation and growth of apatite in SBF for a short time, which indicates a promising way to produce a bone-like apatite coating with high bonding strength on the surface of NiTi SMA by biomimetic growth in SBF. The biomimetic preparation and the bonding characteristics of the apatite coating on the pretreated NiTi SMA as well as further work are being pursued in our laboratory and will be reported in due course.

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