Microstructure, mechanical properties and superelasticity of biomedical porous NiTi alloy prepared by microwave sintering

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ABSTRACT

Porous NiTi alloys were prepared by microwave sintering using ammonium hydrogen carbonate (NH4HCO3) as the space holder agent to adjust the porosity in the range of 22–62%. The effects of porosities on the microstructure, hardness, compressive strength, bending strength, elastic modulus, phase transformation temperature and superelasticity of the porous NiTi alloys were investigated. The results showed that the porosities and average pore sizes of the porous NiTi alloys increased with increasing the contents of NH4HCO3. The porous NiTi alloys consisted of nearly single NiTi phase, with a very small amount of two secondary phases (Ni3Ti, NiTi2) when the porosities were lower than 50%. The amount of Ni3Ti and NiTi2 phases increased with further increasing of the porosity proportion. The porosities had few effects on the phase transformation temperatures of the porous NiTi alloys. By increasing the porosities, all of the hardness, compressive strength, elastic modulus, bending strength and superelasticity of the porous NiTi alloys decreased. However, the compressive strength and bending strength were higher or close to those of natural bone and the elastic modulus was close to the natural bone. The superelastic recovery strain of the trained porous NiTi alloys could reach between 3.1 and 4.7% at the pre-strain of 5%, even if the porosity was up to 62%. Moreover, partial shape memory effect was observed for all porosity levels under the experiment conditions. Therefore, the microwave sintered porous NiTi alloys could be a promising candidate for bone implant.

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1. Introduction

In the past few decades, nearly equiatomic nickel–titanium alloys (NiTi, nitinol) have been considered as excellent biomaterials with potential use in human hard tissue repair and replacement due to their unique properties, such as shape memory effect, superelasticity, good impact resistance and damping, high corrosion resistance and excellent biocompatibility [1–4]. However, one of the most critical issues frequently encountered in hard tissue replacement applications is “stress shielding” generated from the large mismatch of elastic modulus between the hard tissue (<20 GPa) and the implant materials (>100 GPa), which may lead to the resorption of the hard tissue, loosening of the implants and finally, the failure of implantation [5–7]. To solve this problem, introducing pores into the bulk materials and forming the porous materials are the most efficient methods except for developing new lower elastic modulus biomaterials [8–13]. Porous structure could not only provide the adjustable elastic modulus and improve the biomechanical compatibility of the implants, but also allow the ingrowth of new bone tissue and vascularization and a firm fixation of the implants could be obtained. Therefore, porous NiTi alloys have attracted many attentions as implants for hard tissue repair and replacement recently, such as maxillofacial and dental implants, cervical and lumbar vertebral replacements, joint replacements, bone plates, bone tissue engineering, spine fracture fixation, and anchor- and repair [8,9].

Previously several powder metallurgical methods had been employed to fabricate the porous NiTi alloys, including conventional sintering (CS) [14], hot isostatic pressing (HIP) [15], self-propagating high-temperature synthesis (SHS) [16] and spark plasma sintering (SPS) [17]. In recent years microwave sintering technique has emerged as a new sintering method for ceramics, semiconductors, metals and composites [18–20]. Microwave sintering is a process described as follows: the materials, coupled with microwaves, absorb the electromagnetic energy volumetrically, which transforms into heat up to sintering temperature when the densification and alloying are eventually realized [18,19]. As a consequence, compared with conventional sintering, the microwave sintering technique possesses many intrinsic advantages, such as reduced energy consumption, rapid heating rates, reduced sintering times, enhanced element diffusion processes and improved physical and mechanical properties of the sintered materials [18, 19]. Recently, Tang et al. [21] and our preliminary work [22] reported that the porous NiTi alloys could be prepared by microwave sintering,
but the sintered porous NiTi alloys exhibited low porosities and irregular pore size as well as containing many undesired secondary phases (Ni3Ti and NiTi2). In this paper, the biomedical porous NiTi alloys possessing different porosities and regular pore sizes with few second phases were prepared by microwave sintering and space holder technique. At the same time, the effects of porosities on the microstructure, mechanical properties, phase transformation temperatures and superelasticity of porous NiTi alloys were also investigated systematically.

2. Material and methods

Commercially available Ni carbonyl powders (particle size ~2 μm, purity >99.7%) and Ti powders (particle size ~10 μm, purity >99.9%), with a nominal atomic ratio of 50.8 to 49.2, were used to prepare porous NiTi alloy in this experiment. The 120 mesh sieved pure ammonium hydrogen carbonate (NH4HCO3) particles were mixed into the Ni–Ti powders as the space holder agent to adjust the porosities with the contents of 0, 10 wt.%, 20 wt.%, and 30 wt.%, respectively. The mixed Ni(CO)4–Ti–NH4HCO3 powders were blended in a planetary ball mill (QM-3SP4, Nanjing University Instrument Plant) at the speed of 200 r/min for 2 h. The blended powders were cold-pressed into green samples (Φ 20 mm × 15 mm and 6 mm × 6 mm × 50 mm) through a uniaxial pressure of 260 MPa for 30 s. The green compact samples were put into an alumina crucible with SiC particles covering the green sample. Then the alumina crucible was put inside a mullite fiber cotton insulation barrel. The schematic diagram of the insulation barrel setup is shown in Fig. 1. Finally, the insulation barrel was put into a 2.45 GHz 5 kW continuously adjustable microwave equipment (NJZ-3, Nanjing Juequan co., Ltd.). The green compact samples were sintered by microwave heating at a rate of 20–30 °C/min to 1000 °C for 15 min. During the sintering process, the microwave sintering chamber was filled with high purity argon gas flow (99.999%) and a Raytek infrared pyrometer was used to measure the temperature of the sintered samples.

The porous structure of the porous NiTi alloys was investigated by an optical microscope (DM1500, Shenzhen Hipower). The average pore sizes of the porous samples were analyzed by the software of image-pro-plus 6.0 and the general porosity (P) was tested by Archimedes drainage method, calculated by the following formula:

\[ P = 1 - \left( \frac{\rho}{\rho_0} \right) \]  

where \( \rho \) and \( \rho_0 \) represent the density of the sintered porous NiTi alloy and the theoretical density of solid NiTi alloy, respectively; \( \rho/\rho_0 \) is the relative density. In this experiment, the theoretical density (\( \rho_0 \)) was 6.45 g/cm³ [23].

The phase composition of the porous NiTi alloys was identified by X-ray diffraction (XRD, Bruker D8 FOCUS). The phase transformation behavior of the porous NiTi alloys was characterized by using a Perkin-Elmer Diamond differential scanning calorimeter (DSC) with a heating/cooling rate of 20 °C/min, and the phase transformation temperatures extracted from DSC curves were obtained by tangent method using Pyris software. Rockwell hardness of the porous NiTi alloys was measured by HRB-150A Hardness tester with a load of 100 kg for 3 s. Compression test was carried out at an ambient temperature of 25 °C with a constant rate of 0.05 mm/min on Instron WDW-50 testing machine to obtain the compressive strength and elastic modulus of the porous NiTi alloys and with a constant rate of 0.5%/min on Instron 3365 testing machine to investigate the superelasticity of the porous NiTi alloys. At the same time, the three loading-unloading cycle compressive tests under the pre-strain of 5% were carried out (the different pre-strains had been tried, but 5% of the pre-strain was the best to distinguish the superelastic behavior of the porous NiTi alloys with different porosities). The compressive samples were machined into a cylindrical solid with a dimension of Φ 5 mm × 10 mm (L/D = 2.0, ASTM E9-09). The bending tests of the rectangular porous NiTi alloys (5 mm × 5 mm × 45 mm) were carried out at ambient temperature of 25 °C with a constant rate of 0.05 mm/min on Instron WDW-50 testing machine. The bending strength (\( \sigma_b \)) of the porous NiTi alloys could be calculated by the following formula:

\[ \sigma_b = \frac{3FL}{2bh^2} \]

where \( F \) is the maximum loading during testing procedure, \( L \) is the span between two supports and \( b \) and \( h \) represent the breadth and height of the samples, respectively. In this test, the span \( L \) was 30 mm.

3. Results and discussion

Fig. 2 shows the optical micrographs of the porous NiTi alloys prepared by microwave sintering with different contents of NH4HCO3. It could be seen that the number of pores distributed over the surface of the porous NiTi alloys increased with increasing the contents of NH4HCO3. The pores of the porous NiTi alloys without adding NH4HCO3 were isolated and the connectivity among the pores was gradually enhanced as the increase of the NH4HCO3 contents. The average pore sizes of the porous NiTi alloys also increased with increasing the contents of NH4HCO3, shown in Fig. 3. The average pore size of the porous NiTi alloy without adding NH4HCO3 was only 26 μm, while it increased from 120 μm to 178 μm with increasing the NH4HCO3 contents from 10 wt.% to 30 wt.. Especially, the pore size of the sample prepared with 10% NH4HCO3 (120 μm) was consistent with the size of the sieved NiH4HCO3 particles (~120 mesh, ~125 μm). There existed a geometrical heredity effect of space-holder NH4HCO3 particles on the pore shape and size of the porous NiTi alloys [24]. By further increasing the contents of NH4HCO3, the number of pores increased and some of them might connect together, resulting in the increase of the pore sizes, even higher than the size of NH4HCO3 particles.

The porosities and densities of the porous NiTi alloys prepared by microwave sintering with different NH4HCO3 contents are shown in Fig. 4. The porosities of the porous NiTi alloys increased with increasing the contents of NH4HCO3, while the densities decreased. The porosity of the porous NiTi samples without adding NH4HCO3 was only 22%, and it increased from 41% for 10 wt.% NH4HCO3 sample to 62% for 30 wt.% NH4HCO3 sample. On the other hand, the density decreased from 5.03 g/cm³ (0 NH4HCO3 sample) to 2.41 g/cm³ (30 wt.% NH4HCO3 sample), which was lower than those of aluminum and its alloys (~2.7 g/cm³) and very close to the density of human bone (1.8–2.1 g/cm³) [25]. According to the references [26,27], the ideal bone implant materials should have the porosity in the range of 30–90% and the optimal pore size of 100–400 μm. Therefore, the porous NiTi alloy fabricated by microwave sintering had suitable porosity and pore size to become a promising candidate for bone implant.
Fig. 5 shows the XRD patterns of the porous NiTi alloys prepared by microwave sintering with different porosities. The porous NiTi alloys consisted of nearly single B2 NiTi phase with few other impurity phases as the porosities lower than 50%, while the diffraction peaks of the undesired secondary phases Ni₃Ti and NiTi₂ increased by further increasing the porosities. The microwave sintering process, including the greatly enhanced diffusion of the atoms under the microwave field and the quickly derived microwave heating from absorbing the electromagnetic energy volumetrically (which were fundamentally different from the conventional heating derived from the conduction, radiation and convection) [18,19], could accelerate the alloying of the NiTi green compact sample and facilitate its complete reaction, resulting in the formation of nearly single NiTi phase with few secondary phases. After the thermal decomposition of NH₄HCO₃ occurred, the excessive pores were left inside the NiTi green compact sample, which would impede the diffusion of the atoms on a large scale and form the local Ti-rich region and Ni-rich region, resulting in the increase of Ni₃Ti phase and NiTi₂ phase as the porosities higher than 50%. However, the weak diffraction intensity of the Ni₃Ti and NiTi₂ indicated that their contents inside the porous NiTi alloys were limited, much lower than other porous NiTi alloy prepared in the previous references [21–23,28,29]. It is difficult to obtain single NiTi phase for porous NiTi alloy prepared through one-step powder metallurgy methods including CS, HIP, SHS and SPS [8,30,31]. Therefore, it can be concluded that the microwave sintering method is beneficial to reduce, even eliminate the secondary phases (Ni₃Ti and NiTi₂) for the preparation of porous NiTi alloys, which can improve the thermomechanical properties, corrosion resistance and biocompatibility of the porous NiTi alloys [32–34].

Fig. 6 shows the effect of porosities on Rockwell hardness of the porous NiTi alloys. The Rockwell hardness of the porous NiTi alloys abruptly decreased by increasing the porosities, meanwhile its standard deviation gradually increased. The hardness of sample with porosity of 22% could reach 66 HRB, while it decreased by 71% for the sample porosity of 62% (19 HRB). The increase of porosities resulted in the decrease of the support force of pore walls, which inevitably decreased the hardness of the samples.

The compressive stress–strain curves of the porous NiTi alloys with different porosities are shown in Fig. 7 and the compressive strength...
and elastic modulus of the porous NiTi alloys extracted from the stress–strain curves are shown in Fig. 8. An initial stage with low slope appeared in the compressive curves that may be related to experimental instrument and procedure error. By ignoring the initial stage, it could be seen from Fig. 7 that the compressive process could be divided into three regions as follows [35]: (1) a linear elastic deformation region, where the slope could be considered as the elastic modulus of the sample; (2) a plastic yield deformation region, where a peak stress appeared, considered as the compressive strength of the sample; and (3) a densification and rupture region, where the walls of the pores would collapse and the rupture of samples has occurred. It could be clear that the compressive strength and elastic modulus of the porous NiTi alloys decreased by increasing the porosities. The compressive strength and elastic modulus of the sample with porosity of 22% could reach 880 MPa and 7.5 GPa, respectively. By increasing the porosities, they decreased from 319 MPa and 3.91 GPa for the sample with porosity of 41% to 69 MPa and 1.1 GPa, respectively. The elastic modulus of the porous NiTi alloys which ranged from 7.5 GPa to 1.1 GPa was very close to the elastic modulus of natural bone (3–20 GPa for cortical bone and 0.05–0.5 GPa for cancellous bone) [36]. The compressive strength of the porous NiTi alloys which ranged from 880 MPa to 69 MPa was higher or close to the compressive strength of natural bone (100–230 MPa for cortical bone and 2–12 MPa for cancellous bone) [36].

The bending strength is another important mechanical property for the bone implant materials besides the compressive strength and elastic modulus. The bending strength of the porous NiTi alloys with different porosities is shown in Fig. 9. The bending strength of the porous NiTi alloys almost linearly decreased from 371.4 MPa for the sample with porosity of 22% to 74.0 MPa for the sample with porosity of 62% by increasing the porosities, all of which was higher or close to the bending strength of natural cortical bone (50–150 MPa) [36]. Therefore, by only considering the compressive strength, elastic modulus and bending strength, the porous NiTi alloy fabricated by microwave sintering could be a promising candidate for the hard tissue repair and replacement implant.

The effect of porosities on the phase transformation behavior of the porous NiTi alloys is shown in Fig. 10 and the phase transformation temperatures are listed in Table 1. Two exothermic peaks were observed during the cooling process, in which the transformations of B2 phase to R phase and R phase to B19′ phase might occur. On the other hand, only one endothermic peak was detected during the heating process, in which B19′ phase transformed into B2 phase. This result was consistent with the reference [21,23]. According to the DSC curves and Table 1, it was clear that the porosities had few effects on the phase transformation temperatures of the porous NiTi alloys. In general, the phase transformation behavior of the dense NiTi alloys mainly depends on the alloy composition and heat treatment process. In this paper, the composition and heat treatment process of the porous NiTi alloys with different porosities were the same. Therefore, they had the same phase transformation behavior and the same transformation temperatures. On the other hand, the porosities had few effects on the phase transformation temperatures of the porous NiTi alloys.

The stress–strain curves of loading–unloading compressive tests of the porous NiTi alloy with different porosities at pre-strain of 5% are shown in Fig. 11 and the experimental results are shown in Table 2. It
could be seen that the maximum stress and superelastic recovery strains of the porous NiTi alloys decreased by increasing the porosities, while the residual strains increased. Each sample was compressed to the strain of 5% at room temperature, and was then unloaded. After unloading, the residual strains were 0.44%, 1.65%, 1.84% and 2.72% for the samples with porosity of 22%, 41%, 50% and 62%, respectively. On the other hand, the superelastic recovery strains of the samples could be up to 4.56%, 3.35%, 3.16% and 2.28%, respectively. If the compressed samples were heated to 80 °C, higher than the Af, the residual strains of the samples could be recovered to 100%, 75.1%, 63.2% and 37.7%, respectively due to their shape memory effect, which formed the memory recovery strains. Lastly, the total of strain recovery of the porous NiTi alloys, including superelastic recovery strains and memory recovery strains, could be obtained and shown in Table 2. The strain recovery of the porous NiTi alloys also decreased by increasing the porosities.

In order to investigate the effect of training on the superelasticity of the porous NiTi alloys, three loading–unloading cycles were carried out. The cycling stress–strain curves of the porous NiTi alloys with different porosities are shown in Fig. 12. After three loading–unloading cycles, all of the stress–strain curves turned into closed loops, in other words, the samples exhibited nearly complete superelasticity. The superelastic recovery strains of the porous NiTi alloys could reach 4.7%, 4.4%, 4.0% and 3.1% for the samples with the porosity of 22%, 41%, 50% and 62%, respectively. The results were higher than those of the above-mentioned values, indicating that training could greatly improve the superelasticity of the porous NiTi alloy, consistent with other references [21,37]. However, the superelasticity of the trained porous NiTi alloys was also lower than the pre-strain of 5%. It is well known that the dense bulk NiTi alloy can recover up to 8% strain in uniaxial deformation by a reversible stress-induced martensitic transformation [1,2]. However, when the porous NiTi alloy was deformed to 5%, the certain local strain might be higher than 8% due to the stress concentration generated from the large number of pores or other defects inside the porous NiTi alloy. Therefore, the porous NiTi alloy is difficult to possess the actually complete superelasticity or shape memory effect even with training.

The porous NiTi alloys exhibiting excellent superelasticity (~3%) can greatly match the natural bone which has a recoverable strain around 2% [1,4,37]. This mechanical characteristic of the porous NiTi alloy is incomparable for other metallic biomaterials, such as Ti, Ti–6Al–4V, stainless steels, and Co based alloys. Moreover, the unique property should obtain easier deployment of porous NiTi into the implantation site. With the combination of the porosity, pore size, relatively pure phase composition, mechanical properties, shape memory effect and superelasticity, it could be concluded that the porous NiTi alloys prepared by microwave sintering using ammonium hydrogen carbonate as the space holder agent should become a promising candidate for bone implant.

<table>
<thead>
<tr>
<th>Porosity (%)</th>
<th>Cooling process</th>
<th>Heating process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rs °C</td>
<td>Rf °C</td>
</tr>
<tr>
<td>22</td>
<td>18.0</td>
<td>7.3</td>
</tr>
<tr>
<td>41</td>
<td>20.1</td>
<td>7.9</td>
</tr>
<tr>
<td>50</td>
<td>21.4</td>
<td>7.7</td>
</tr>
<tr>
<td>62</td>
<td>19.4</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Fig. 9. Relationship between porosity and bending strength of the porous NiTi alloys.

Fig. 10. DSC curves of the porous NiTi alloys with different porosities: (a) heating and (b) cooling.

Fig. 11. Stress–strain curves of loading–unloading compressive tests of the porous NiTi alloy with different porosities at the pre-strain of 5%.
4. Conclusions

(1) Porous NiTi alloys were successfully prepared by microwave sintering and space holder technique. The porosities of the porous NiTi alloys increased from 22% to 62% by increasing the contents of NH₄HCO₃ and the corresponding average pore size increased from 26 μm to 178 μm.

(2) The porous NiTi alloys consisted of nearly single NiTi phase with few secondary phases as the porosities lower than 50%, while the Ni₃Ti phase and NiTi₂ phase increased by further increasing the porosities.

(3) The porosities had few effects on the phase transformation temperatures of the porous NiTi alloys. Partial shape memory effect was observed for all porosity levels and the porosities had adverse effect on the shape recovery.

(4) By increasing the porosities, all of the hardness, compressive strength, elastic modulus, bending strength and superelasticity of the porous NiTi alloys decreased. The superelasticity of the porous NiTi alloys could be improved through training.

Acknowledgments

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References


Table 2

Results of loading–unloading compressive tests of the porous NiTi alloys with different porosities.

<table>
<thead>
<tr>
<th>Porosity (%)</th>
<th>Maximum stress (MPa)</th>
<th>Superelastic recovery strain (%)</th>
<th>Residual strain (%)</th>
<th>Memory recovery strain (%)</th>
<th>Strain recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>191.1</td>
<td>4.56</td>
<td>0.44</td>
<td>0.44</td>
<td>5.00</td>
</tr>
<tr>
<td>41</td>
<td>169.5</td>
<td>3.35</td>
<td>1.65</td>
<td>1.24</td>
<td>4.59</td>
</tr>
<tr>
<td>50</td>
<td>114.8</td>
<td>3.16</td>
<td>1.84</td>
<td>1.17</td>
<td>4.33</td>
</tr>
<tr>
<td>62</td>
<td>44.3</td>
<td>2.28</td>
<td>2.72</td>
<td>1.03</td>
<td>3.31</td>
</tr>
</tbody>
</table>

Fig. 12. The cycling stress–strain curves of the porous NiTi alloys with different porosities: (a) 22%; (b) 41%; (c) 50%; and (d) 62%.