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Porous Ni-Ti Shape Memory Alloys Produced by Two Different Methods

Porous Ni-Ti shape memory alloys (SMAs) have been successfully produced by self-propagating high-temperature synthesis (SHS) and conventional powder sintering. The alloys produced by these two methods have very different characterization of pore structure, fracture mechanism and DSC profiles. Moreover, it is easy to produce bulk samples of porous Ni-Ti SMAs by SHS and the pre-heating temperature is very important for successful preparation of porous Ni-Ti SMAs. Pre-heating temperature between 150°C and 550°C is suitable in the present study.

1 Introduction

There are now 500,000 hip replacements per annum world-wide. The use of prosthesis in joint replacement is, and will continue to be, a rapidly expanding part of the surgical field. The major problem with current joint replacements is aseptic loosening due to poor bone integration around the implant and different mechanical deformation behavior between the implant and the replaced bone. Therefore, extra surgical revision is necessary and new biomaterial should be used. It has been found that the mechanical deformation behavior of bone and other biological materials, which have a high recoverable strain ($\geq 2\%$, Fig. 1), is quite different from that of common metallic materials and only the pseudoelasticity of shape memory alloys (SMAs) is similar in this aspect [1]. The open porous structure of porous materials is particularly suitable for implant fixation through tissue rapid ingrowth which offering distinct advantages over other methods for achieving secure tissue-to-implant fixation [2]. Moreover, Ni-Ti SMAs have excellent mechanical properties, good corrosion resistance, high biocompatibility and special shape memory effect. Therefore, porous Ni-Ti SMAs have been recently acknowledged as promising biomaterials for bone prosthesis and repair.

There are several reports about the preparation of Ni-Ti

10²MPa



Fig. 1. Stress-strain behavior of different biological materials [1]. 1. Hair; 2. Bone; 3. Bone glue; 4. Birch; 5. Poplar.

SMAs by self-propagating high-temperature synthesis (SHS) [3 to 5] and conventional powder sintering (CPS) [6 to 8]. Between the two different methods, the SHS technique attracts especial attention due to its cost- and time- effectiveness. However, most of reports focus on obtaining dense alloys but not on porous ones. Thus, the lack of comprehensive studies on the porous Ni-Ti SMAs produced by SHS and CPS is one main motivation of this paper.

2 Experimental

In the present study, two methods, i.e., SHS and CPS, are performed to produce porous Ni-Ti SMAs. In the SHS method, the reactant powders of Ti and Ni were mixed at the Ni and Ti equiatomic composition. The green compacts, whose porosity was about 58 vol.%, were then put into a tube furnace with certain pre-heating temperature and ignited. The details about the CPS method were described in the literature [9]. In the CPS method, Ti, Ni and TiH₂ were mixed also at Ni/Ti equiatomic composition (Table 1), the green compacts with porosity in the range of 47.7-50.1 vol.% were isothermally sintered at 950°C for 9hrs in a vacuum tube furnace.

The general porosity was determined by weight and dimensional measurements, and the open porosity was measured by the liquid weighing method. The open-pore ratio is defined as the ratio of the open porosity to the general porosity.

In order to monitor the temperature distribution in the combustion samples, Pt-Rh thermocouple was inserted into the drilled wells in the green compacts. X-ray diffraction (XRD), scanning electron microscopy (SEM), IPS-500 Image Analysis and differential scanning calorimeter (DSC) were used to analysis the microstructure and phase transformation.

3 Results and Discussion

Porous Ni-Ti SMAs have been successfully produced by SHS and CPS. The microstructure, characterization of pore, phase composition and fracture behavior of porous Ni-Ti produced

Table 1. Chemical composition of blended powders used in CPS (wt.%).

Sample	Chemical Composition (wt. %)				
No.	Ti	TiH ₂	Ni		
1	44.9	0.0	bal.		
2	35.8	9.3	bal.		
3	17.8	27.8	bal.		
4	0.0	45.9	bal.		



Fig. 2a. XRD results of porous Ni-Ti SMAs prepared by SHS.

by these two methods have been investigated.

3.1 Phase Composition of Porous Ni-Ti SMAs

Figures 2a and b show the X-ray analysis of porous Ni-Ti SMAs synthesized by SHS and CPS, respectively. It can be found that 100% Ni-Ti intermetallics have been achieved using both methods and there always exist B2(NiTi), B19(NiTi), Ni₃Ti and Ti₂Ni, and B2(NiTi) is the dominant phase. Looking at the phase diagram of Ni-Ti alloy (Fig. 3), one can see that Ni₃Ti, Ti₂Ni and NiTi are three stable phases in Ni-Ti alloys, and Ni₃Ti and Ti₂Ni are more thermodynamically favored to form than NiTi. Therefore Ni₃Ti and Ti₂Ni are difficult to be inhibited completely by the sintering methods and NiTi is the dominant phase due to the Ni/Ti equiatomic composition.

3.2 Porosity, Pore Size and Pore Distribution

In a porous material, the pores have different shapes (Fig. 4) and therefore different influences on the materials properties. It has been suggested [10] that the following parameters have to be investigated for the characterization of pore structure: (i) general porosity, (ii) open porosity, (iii) the percentage of open porosity representing the channel (permeable pores; see Fig. 4),



Fig. 3. The Ni-Ti phase diagram.



Fig. 2b. XRD results of porous Ni-Ti SMAs produced by CPS.

i.e., open-pore ratio, and (iv) channel/pore size.

The general porosity, open porosity, open-pore ratio and pore size of porous Ni-Ti SMAs are listed in Tables 2 and 3. Compared with the green porosity, one can see that the porosity before combustion/sintering has increased after SHS while decreased after CPS. Moreover, The alloys produced by SHS have high porosity, high open-pore ratio and big channel sizes (in the order of 400µm). And the alloys produced by CPS have relatively low porosity while also high open-pore ratio and the corresponding pore sizes are smaller than 100µm. It should be noted that porosity and high open-pore ratio are very important for biomedical materials used as bone implants because suitable porosity with high open-pore ratio allows natural bone re-growth to occur until complete intimate contact has been achieved between the natural bones and the porous implants. In addition, according to the literature [4], there exists an optimal pore size and porosity range for implant materials. Normally, with porosity in the range of 30-90%, the optimal pore size for bone tissue ingrowth is 100~500µm and that for connective fibrous tissue ingrowth is smaller than 100µm. Therefore, it seems that the present porosity and channel size can meet these requirements.

The optical micrographs of porous Ni-Ti SMAs are shown in Figs 5a and b. As can be seen, the porous Ni-Ti SMAs produced by SHS have a three dimensionally interconnected porous structure, and the alloys produced by CPS have homogeneous pore distribution whereas their pores are small and in irregular shapes.



Fig. 4. Principal pore shapes.

Pre-heating temperature, °C	400	450	500	525	550
General porosity, %	60.6	58.0	61.1	60.8	
Open porosity, %	58.2	57.2	59.2	58.1	
Open-pore ratio, %	96.0	98.6	96.9	95.6	
Channel size, mm		0.32	0.35	0.45	
Pore size, mm		0.12	0.05	0.07	

Table 2. Characterization of pore structure of alloys prepared by SHS.

Table 3. The characterization of pore structure of alloys produced by CPS.

Sample No.	1	2	3	4
General porosity, %	36.0	36.3	35.9	32.6
Open porosity, %	35.9	35.7	34.6	31.3
Open-pore ratio, %	99.6	98.3	96.5	95.9
Pore size, mm	0.095	0.092	0.068	0.061

The aforementioned porous structure and the difference of porosity change before and after combustion/sintering can be explained by the sources of pores in porous Ni-Ti SMAs:

- (1) Initial porosity of the reactant body;
- (2) Heterogeneous phases (such as Ti_2Ni , Ni_3Ti , and Ni_4Ti_3) formation due to the different diffusion rates of Ti and Ni, e.g., at 950°C the bulk diffusion rates of Ti and Ni are 2.0×10^{-10} and 1.5×10^{-12} cm²/s respectively, leading to generation of Kirkendall pores;

- (3) Pores generated because of the molar volume change from reatants to products;
- (4) Soret effect due to the thermal migration in the large temperature gradients during combustion;
- (5) Outgassing of adsorbed gasses and evaporation of volatile impurities occurring at high temperatures of combustion.

Obviously, the initial porosity of the reactant body is the main origin of the final porosity, which forms a porous structure, in the alloys produced by both methods. The porosity as results of (1)~(3) contributes to the pores in the alloys produced by both methods. However, compared to the CPS method, the contribution of (4) and (5) due to the high thermal gradients during combustion is an extra origin of pores to the alloys produced by SHS, and this contribution is probably the main reason for the big channels and the increase of porosity during SHS.

3.3 The Temperature Profiles Analysis in SHS

Figures 6a and b are the macrographs of porous Ni-Ti SMAs



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Figs 5a and b. Optical micrographs of porous Ni-Ti SMAs produced by (a) SHS and (b) CPS.

Figs 6a and b. Macrograph (a) of porous Ni-Ti SMAs prepared by SHS at different pre-heating temperatures. Macrograph (b) is a higher magnification, which shows an obvious melting, of the product prepared at pre-heating temperature of 550°C in (a).

a)



Fig. 7. Typical temperature profiles in SHS.

produced by SHS. It can be found that the alloy produced at pre-heating temperature of 550°C has melted obviously during combustion (see Fig. 6(b)). This means that the pre-heating temperature to produce porous Ti-Ti SMAs should not exceed 550°C. The typical temperature-time profiles during combustion are shown in Fig. 7. The green compacts are ignited at certain pre-heating temperature (T_0) and the combustion wave propagates toward the location of the thermocouple. As the combustion wave reaches the location of the thermocouple, the temperature increases sharply, reaching the maximum temperature, i.e., combustion temperature (T_c), in a short time (tens of seconds). After that, the thermocouple records the cooling of the products.

The combustion does not occur at pre-heating temperature of 153°C, this is due to the low heat provided by pre-heating and the low exothermicity of the reaction between Ni and Ti. However, further increased the pre-heating

temperature (for example, 203°C and 354°C), the combustion can easily be ignited. Moreover, with increasing pre-heating temperature, the combustion temperature increases. This can be explained by the mechanism of combustion. During combustion, the following reaction mainly takes place:

$$Ni+Ti \rightarrow NiTi+67kJ/mol$$
(1)

With the heat released from the above reaction and the heat provided by pre-heating, the combustion becomes self-sustaining. Assuming that the enthalpy of the reaction heats up the products and that no energy is lost to the surrounding environment, and the adiabatic temperature (T_{ad}) can be taken as combustion temperature (T_c) . Then, the combustion temperature can be approximately calculated from the heat balance condition [11]

$$-\Delta H_{T_0} = -\Delta H_{298} + \int_{298}^{T_0} (C_{p,Ni} + C_{p,Ti}) dT$$
$$= \int_{T_0}^{T_c} C_{p,NiTi} dT$$

where ΔH_{T_0} , ΔH_{298} are the enthalpies of the aforementioned reaction (1) at pre-heating temperature (T₀) and ambient temperature (25°C). $C_{p,Ti}$, $C_{p,Ni}$, and $C_{p,NiTi}$ are the heat capacities of the Ti, Ni and NiTi alloy, respectively. Obviously, the enthalpy of reaction (ΔH_{T_0}) is an important parameter which decides whether or not a chemical reaction is self-propagating. At low pre-heating temperature, the enthalpy change is low, no combustion can occur. In the present study, pre-heating at or below 153°C can not supply enough enthalpy for combustion to self-propagating, therefore the combustion does not occur. With further increasing pre-heating temperature to 203 or 354°C, the enthalpy of reaction (ΔH_{T_0})



Fig. 8. SEM micrographs of fractured porous Ni-Ti SMAs prepared by SHS.

Fig. 9. SEM micrographs of fractured porous Ni-Ti SMAs produced by CPS.



Fig. 10. Typical DSC curve of porous Ni-Ti SMAs prepared by SHS at pre-heating temperatures of 400°C and 525°C.

increases to enough high and thus the combustion occurs with self-propagating and T_c also increases. When pre-heating temperature is enough high (for example, 550°C), the great enthalpy of reaction makes the T_c exceed the melting temperature of NiTi phase and melting occurs (see Fig. 6c).

3.4 Fractography

In the present study, post-fracture observations have been conducted to identify the failure mechanisms of porous Ni-Ti SMAs. Figs 8 and 9 represent the fractographs of porous Ni-Ti SMAs produced by SHS and CPS, respectively. It can be found that the alloys prepared by SHS fracture in a ductile failure mode while those produced by CPS fail in a mixed cleavage and ductile failure mode. Moreover, the fracture morphologies of alloys synthesized by SHS exhibit a dimple network with dimples of various sizes and shapes, and secondary cracks can be easily observed.

3.5 The DSC Curves of Porous Ni-Ti SMAs

Figures 10 and 11 represent the typical DSC curves of porous Ni-Ti SMAs produced by SHS and by CPS, respectively. One can see that two-peak phenomenon appears in both heating and cooling in the DSC curve of porous Ni-Ti alloys produced by CPS due to the microcompositional fluctuation [12]. Whereas this phenomenon does not occur in the alloys prepared by SHS. Therefore, the alloys produced by SHS have more uniform composition distribution due to the high thermal gradients, high combustion temperature and possibly existed melting during combustion.

4 Conclusions

Porous Ni-Ti SMAs produced by SHS and CPS have very different porosity and channel/pore sizes, their corresponding fracture behavior and DSC curves are also different. The porous Ni-Ti SMAs produced by SHS show a ductile failure



Figs 5a and b. Optical micrographs of porous Ni-Ti SMAs produced by (a) SHS and (b) CPS.

mode, while those alloys produced by CPS fail in a mixed cleavage and ductile failure. The DSC curves show that the alloys produced by SHS have more uniform composition distribution than those produced by CPS.

Further, it is easy to produce bulk samples of porous Ni-Ti SMAs with a three-dimensionally open porous structure by SHS. The pre-heating temperature is very important for successful preparation of porous Ni-Ti SMAs. It is found that the pre-heating temperature should be higher than 150°C and lower than 550°C because the combustion does not self-propagate at pre-heating temperature of 153°C and obvious melting occurs at pre-heating temperature of 550°C.

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