Effect of Preheating Temperature and chamber Pressure on the Properties of Porous NiTi Alloy Prepared by SHS Technique

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Abstract—The fabrication of porous NiTi shape memory alloys (SMAs) from elemental powder compacts was conducted by self-propagating high temperature synthesis (SHS). Effects of the preheating temperature and the chamber pressure on the combustion characteristics as well as the final morphology and the composition of products were studied. The samples with porosity between 56.4 and 59.0% under preheating temperature in the range of 200-300°C and Ar-gas chamber pressure of 138 and 201 kPa were obtained. The pore structures were found to be dissimilar only in the samples processed with different preheating temperature. The major phase in the porous product is NiTi with small amounts of secondary phases, $NiTi_2$ and Ni_4Ti_3. The preheating temperature and the chamber pressure have very little effect on the phase constituent. While the combustion temperature of the sample was notably increased by increasing the preheating temperature, they were slightly changed by varying the chamber pressure.

Keywords—Combustion synthesis, Porous materials, Self-propagating high temperature synthesis, Shape memory alloy

I. INTRODUCTION

SELF-PROPAGATING high temperature synthesis (SHS) is well known to be an attractive alternative to the conventional methods for synthesizing many porous intermetallic compounds, including carbides, borides, nitrides, hydrides, etc [1]. The synthesis occurs in a single process step within short processing times (few seconds to few minutes) at high reaction temperature (1500-4000°C). The resultant alloy is homogeneous with the desirable stoichiometry. This eliminates the subsequent thermo mechanical processing for homogenization [2]. With the advantages of time and energy savings, SHS is therefore a suitable production method for synthesizing porous NiTi SMAs.

The porous NiTi SMAs have received a significant attention in the biomaterials field research due to their excellent mechanical properties, unique shape memory effect and superelasticity, good corrosion resistance, superior damping capability, good biocompatibility and good porous structure [3-4]. Porous NiTi with interconnected pores and pore size in the range of 100-500 μm are desirable since it allows human tissues to grow inside and body fluids to be circulated through the interconnected pores.

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For the fabrication of porous NiTi SMAs by the SHS from the elemental powders, the chemical reaction is weakly exothermic. It is therefore necessary to preheat the sample prior to sample ignition to achieve a self-sustained combustion [2, 6-8]. With this mode of combustion, highly porous NiTi alloy at 60% porosity has been produced [9]. Chu et al. has also successfully fabricated the porous NiTi SMA with homogeneously distributing spherical pores with the porosity of 70% by SHS [10]. However, most pores in his porous samples are not open.

Based on our previous work [8], the compact pressure was observed to have a significant effect on the average size, numbers and shapes of pores. It is the objective of the present work to further experimentally investigates the effects of the preheating temperature and the chamber pressure on the morphology and phase evolution of combustion products.

II. EXPERIMENTAL METHODS

The starting materials used were commercial high-purity powder of Ni (99.8%) and Ti (99.5%) supplied by Alfa Inc., USA. The average particle sizes of Ni and Ti are 16.4 μm and 34.9 μm respectively. The mixed powders of Ni and Ti with equiatomic stoichiometry were blended by a planetary ball mill for 12 hours under an atmosphere of argon, and then cold-pressed into a cylindrical sample with a diameter of 14 mm and a height of 28 mm at compaction pressure levels of 8 MPa. The compacted specimen was then placed in the chamber and type K thermocouple (Omega Inc.) was attached onto the upper surface of the specimen in order to measure the combustion temperature of powder compact. The temperature-time profiles were recorded by using a USB Data Acquisition recorder. The SHS experiments were conducted in the chamber under an atmosphere of argon at a pressure of 138 kPa and 201 kPa. The preheating temperatures used in this study were 200°C, 250°C and 300°C. The preheated compact was ignited at one end by tungsten coil in a furnace. The general porosity of the specimens was calculated by the formula

$$\varepsilon = \left(\left[1 - \frac{\rho}{\rho_o} \right] \times 100 \right)$$

in which ρ and ρ_o are the density of the specimen and its corresponding theoretical density, respectively. The density and the open porosity of the specimen were determined by the liquid weighing method [11]. The theoretical density value is 6.44 g/cm^3 for the NiTi alloy.

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After reaction, the microstructural characteristic of products was examined under an optical microscope and a scanning electron microscope (SEM). The phase constituents were identified by an X-ray diffraction (XRD).

III. RESULTS AND DISCUSSION

The effects of a preheating temperature and a chamber pressure on the combustion temperature, pore morphology, and phase evolution are described below:

A. Influence on the combustion temperature

Table I shows the combustion temperature of the samples synthesized at different preheating temperatures of 200°C, 250°C and 300°C, and different chamber pressures of 138 kPa and 201 kPa. It can be observed in Table 1 that the combustion temperature increases with increasing the preheating temperature, and reaches the maximum temperature of 749°C at a preheating temperature and a chamber pressure of 300°C and 138 kPa, respectively. This highest combustion temperature is below the lowest eutectic temperature (942°C) of the Ni-Ti mixture and below the melting point of the NiTi alloy (1310°C). Therefore no liquid possibly exists, and solid-state reaction is the dominant mechanism. The original pores in the green compact are hence the main origins of pores obtained in the final products.

An increase in a combustion temperature with increasing a preheating temperature can be explained by thermodynamics calculation [7] . Li and co-workers [7] reported that a higher preheating temperature results in a higher enthalpy of formation and hence a higher adiabatic combustion temperature and a minimum preheating temperature required for the SHS of Ni-Ti system is 150°C. On the other hand, a higher chamber pressure results in a lower combustion temperature as illustrated in Table I. This is due to the decreases in the enthalpy of formation and the adiabatic combustion temperature [12]. However, the effect of the chamber pressure on a combustion temperature is smaller than the effect of the preheating temperature as the enthalpy of formation is more sensitive to the preheating temperature.

TABLE I
EFFECT OF PREHEATING TEMPERATURE AND CHAMBER PRESSURE ON THE COMBUSTION TEMPERATURE OF SAMPLE COMPACTS AT 8 MPA

Preheating temperature (°C)	Argon gas pressure in reactor	
	138 kPa Combustion temperature (°C)	201 kPa Combustion temperature (°C)
200	703 ± 13	696 ± 13
250	730 ± 18	723 ± 13
300	749 ± 11	744 ± 10

B. Influence on pore morphology

Table II shows the porosity information of the reacted samples. As pointed out by Munir and Wang [13], pores in SHS-reacted products have five possible sources. They are: (1) existing pores in the reactants prior to combustion; (2)

differences in molar volume between reactants and products; (3) differences in diffusion rates between nickel and titanium; (4) gas evolution during reaction; and (5) thermal migration due to the high temperature gradient during combustion. Certainly, the first one is the main contribution since the reactants prior to combustion have a green porosity of 54.7 vol.% which are closed to the porosity levels of the synthesized products (56-58 vol.%), as observed in Table II. It is also noted in Table II that most pores are interconnected as indicated from the open porosity ratio, which is in excess of 0.89. Porous NiTi SMA with such pore characteristics is suitable for use as hard tissue implants [14].

TABLE II
TOTAL POROSITY, OPEN POROSITY AND OPEN POROSITY RATIO OF SYNTHESIZED SAMPLES AT DIFFERENT SHS CONDITIONS

Preheating temperature (°C)	Argon gas pressure in reactor (KPa)	Total porosity (vol.%)	Open porosity (vol.%)	Open porosity ratio (vol.%)
200	138	57.9	55.8	0.96
	201	58.0	56.9	0.98
250	138	56.8	55.4	0.98
	201	57.2	55.6	0.97
300	138	56.2	52.4	0.93
	201	56.1	50.2	0.89

Fig. 1, the micrographs of porous NiTi SMAs produced by SHS, demonstrates the porous nature of the SHS products. Figs. 1(a) to 1(c) and Fig. 1(d) to 1f show two series of longitudinal sections of porous parts synthesized at 138 kPa and 201 kPa, respectively, with various preheating temperature. Although linearly aligned channels in longitudinal sections were observed by Li et al. [7], here we obtained striations in the range of 1 to 4.5 mm long along the transverse direction and perpendicular to the direction of the combustion wave front during SHS. This was similar to another work by Tay et al. [2]. When a higher preheating temperature of 300°C was used, the orientation of the striations also appeared to divert longitudinally from a transverse direction. Furthermore, with increasing a preheating temperature, the distance between each striation was wider and hence the porosity was reduced, as collaborated in Table II. The change in pore morphology results from a higher flame-front velocity owing to a higher combustion temperature at a higher preheating temperature. A chamber pressure, however, shows almost no effect on pore morphology of the synthesized samples as can be seen in Fig. 1.

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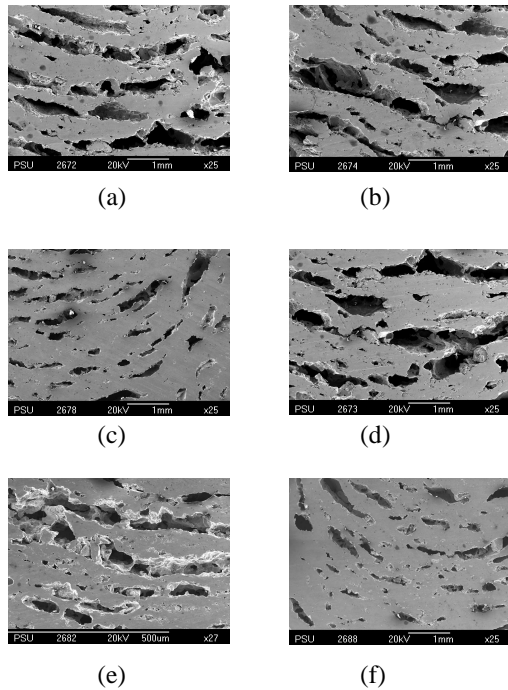
(a)   (b)

(c)   (d)

(e)   (f)

Fig. 1 Longitudinal views of SHS synthesized parts at different preheating temperatures and different chamber pressures: (a) 200°C, 138 kPa, (b) 250°C, 138 kPa, (c) 300°C, 138 kPa, (d) 200°C, 201 kPa, (e) 250°C, 201 kPa, (f) 300°C, 201 kPa

C. Influence on phase evolution

Fig. 2 shows an XRD pattern of the mechanically alloying Ni-Ti powders. As can be seen the nickel and titanium powders have been only mechanically mixed without no alloying. XRD patterns of the SHS-synthesized porous NiTi SMAs at the chamber pressure of 138 kPa and 201 kPa under different preheating temperatures are shown in Fig. 3 and 4, respectively. It can be observed from the XRD spectrum (Fig. 3 and 4) and Table III that there is no significant effect of the chamber pressure and the preheating temperature on phase evolution. The SHS process results in the formation of several intermetallic compounds, such as NiTi, $NiTi_2$ and Ni_4Ti_3. The B2(NiTi) and B19'(NiTi), which are the desired products, are the predominant phases in the reacted samples. It is common to find the presence of the second phases in the products processed by SHS because of the compositional fluctuation in the specimen. This is due to the raw powders were insufficiently mixed and the particle size of the reactants is not small enough which make it impossible for nickel and titanium particles to meet one by one [15]. Among these compounds, NiTi and $NiTi_2$ are stable phases while Ni_4Ti_3 is a metastable phase in NiTi system. The presence of the Ni_4Ti_3 phase corresponds to can be explained as follows. The formations of $NiTi_2$ in the samples make the parent NiTi phase more Ni-rich [14], and give rise to an opportunity for Ni_4Ti_3 to form during the reaction.
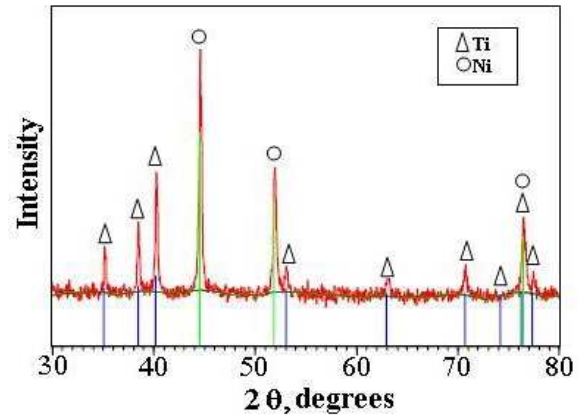

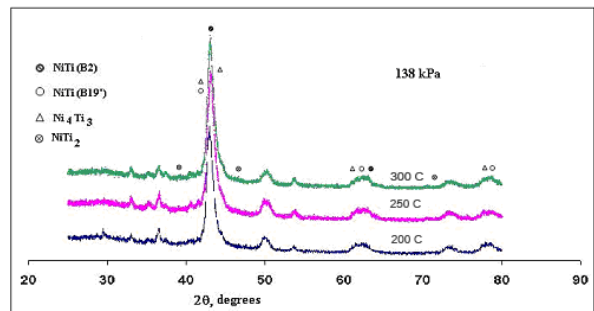Fig. 2 XRD pattern of the mechanically alloying Ni-Ti powders

Fig. 3 XRD patterns of the SHS-synthesized porous NiTi SMAs at a chamber pressure of 138 kPa with different preheating temperatures of 200°C, 250 °C and 300°C
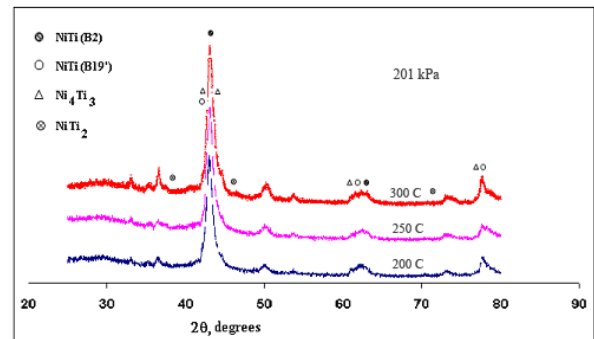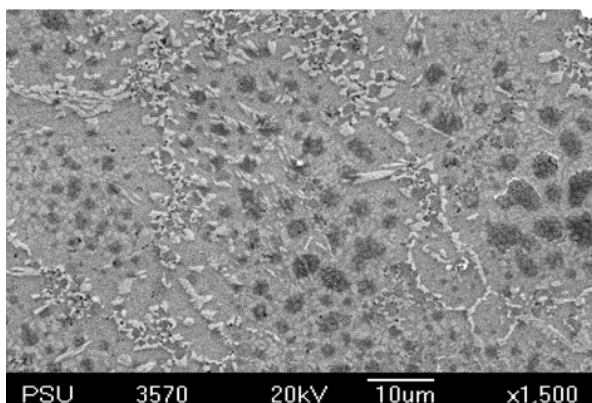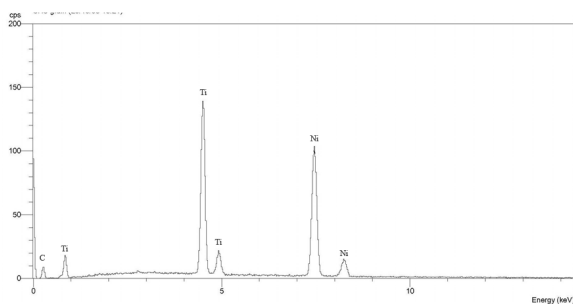

Fig. 4 XRD patterns of the SHS-synthesized porous NiTi SMAs at a chamber pressure of 201 kPa with different preheating temperatures of 200°C, 250 °C and 300°C
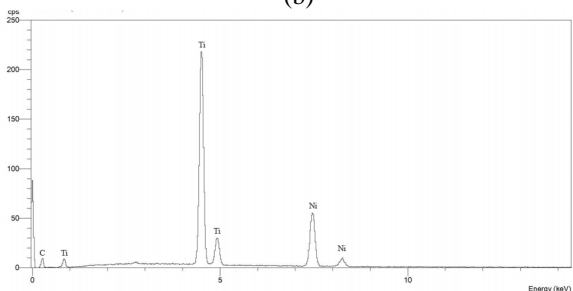
Fig. 5 show the SEM micrographs and EDS analysis of the sample synthesized at a preheating temperature and a chamber pressure of 250°C and 138 kPa, respectively. It can be seen from Fig. 5(a) that the matrix of the sample is NiTi with the discrete (lighter color in Fig. 5(a)) particles of $NiTi_2$ forming along the grain boundary of NiTi. However, Ni_4Ti_3 was not observed in this figure due to very small size of the metastable phase. The EDS analysis from the NiTi matrix and one of $NiTi_2$ particles are shown in Fig. 5(b) and 5(c).

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(a)

(b)

(c)

Fig. 5 (a) SEM micrograph , (b) EDS analysis from NiTi matrix and (c) EDS analysis from $NiTi_2$ of the SHS sample with a preheating temperature and a chamber pressure of 250 °C and 138 kPa, respectively

IV. CONCLUSIONS

The study on the effects of a preheating temperature and a chamber pressure on the combustion temperature, pore morphology, and phase evolution of NiTi SMAs synthesized by the SHS technique leads to the following important conclusions.

The combustion temperature is found to increase with increasing preheating temperature and the maximum combustion temperature recorded in this study was 749°C. The higher the chamber pressure, however, results in the lower the combustion temperature.

Of these two factors, the preheating temperature shows a greater impact on the combustion temperature than the chamber pressure.

Porous NiTi SMAs samples have the average pore size in the range of 368-497 μm with the total porosity and the open porosity ratio of 56-58 vol.% and 89-98%, respectively. The primary source of porosity in the synthesized samples was attributed to the sample green porosity. A higher preheating temperature results in the change in pore morphology as the orientation of pores appears to divert to a vertical direction and the porosity is decreased. A chamber pressure, however, has almost no effect on pore morphology.

The desired products, such as B2(NiTi) and B19'(NiTi) are the predominant phases in the porous NiTi SMA. In addition, the SHS process results in the formation of other second phases, such as $NiTi_2$ and Ni_4Ti_3. The appearances of $NiTi_2$ phase often occurs on or near grain boundaries of NiTi matrix.

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