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A study on microstructure and porosity of NiTi alloy implants produced by SHS

Gul Tosun [a,*], Latif Ozler [b], Mehmet Kaya [c], Nuri Orhan [d]

[a] Firat University, Technical Vocational School, 23119 Elazig, Turkey
[b] Firat University, Engineering Faculty, Mechanical Engineering Department, 23119 Elazig, Turkey
[c] Adiyaman University, Vocational School, 02040 Adiyaman, Turkey
[d] Firat University, Technical Education Faculty, Metal Education Department, 23119 Elazig, Turkey

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ABSTRACT

In this study, Ni and Ti with 50.5 at.% Ni powders were blended for 12 h and cold pressed in the different pressures (50, 75 and 100 MPa). Then, the porous NiTi alloy compacts obtained were synthesized by SHS (self-propagating high-temperature synthesis) at the different preheating temperatures (200, 250 and 300 °C) and heating rates (30, 60 and 90 °C/min). The effects of the pressure, preheating temperature and heating rate were investigated on the porosity and the microstructure. NiTi was seen as the dominant phase in the microstructure with other secondary intermetallic compounds. The porosity of the synthesized products was in the range of 50.7–59.7 vol.%.

1. Introduction

Biomaterial is a nonviable material used in medical devices and artificial organs to interact with biological systems. With developments in medicine area, biomaterials are widely used to standby organ instead of certain organs of human body not to function with reasons such as various illness, accidents and old age. The biomaterials industry worldwide has an annual turnover of $2.3 billion in the field of hard-tissue repair and replacement. There has been and will continue to be a growing need for such biomaterials. However, common biomaterials can result in various problems usually related to the mismatch between the implant and the replaced bone. When an implant due to its physicochemical and mechanical properties is rejected, it is not in good and permanent contact with body tissues [1]. Porous NiTi shape memory alloys (SMAs) are materials widely used in numerous biomedical applications (orthodontics, cardiovascular, orthopedics, urology, etc.) due to their good biocompatibility, unique shape memory properties, mechanical properties, superior damping capability, excellent corrosion resistance and wear resistance [2–5]. Moreover, the porous NiTi alloy shows promising potential in the application of bone implantation because the porous structure allows the ingrowths of new bone tissue along with the transport of body fluids, thus ensuring a harmonious bond between the implant and the body [3].

Porous NiTi SMAs have been fabricated with powder metallurgy (PM) processes such as self-propagating high-temperature synthesis (SHS), metal injection molding (MIP), hot isostatic pressing (HIP) and spark plasma sintering (SPS) [3,4,6–9]. These processes can avoid the problems associated with casting, like segregation or extensive grain growth and have the added advantages of precise control of composition and easy realization of complex part shapes [8]. As a result, compared with traditional methods, self-propagating high-temperature synthesis (SHS) has the advantages of time and energy savings, and is being studied extensively for the fabrication of ceramic and intermetallic compounds [10].

In this study, porous NiTi alloy implants with 50.5 at.% Ni was produced by SHS under the different process parameters such as preheating temperature, heating rate and pressure. The effect of these process parameters on the microstructure and porosity of NiTi alloy implants were experimentally investigated.

2. Experimental procedure

Titanium and nickel powders were used to produce porous NiTi alloy implants. The characteristic features of powders used are shown in Table 1. The mixed powders of Ni and Ti with 50.5 at.% Ni were blended for 12 h and then cold pressed in a cylindrical die with 10 mm diameter under different compaction pressures (50, 75 and 100 MPa) using a hydraulic press. The cold compacted samples with green porosity were heated under different heating rates (30, 60 and 90 °C/min) with the protection of high purity argon gas (99.9%) of about 0.1 MPa in a furnace (Fig. 1). The samples were ignited under different preheating temperatures (200, 250 and 300 °C) using electrical discharge pulse (14 kV and 30 mA). Once ignited, combustion waves could self-propagate along the axis to the other end of the compact in a very short time, and then porous NiTi implants were obtained by synthesizing.

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* Corresponding author. Tel.: +90 424 2370000; fax: +90 424 2415526.
E-mail address: gultosun@firat.edu.tr (G. Tosun).

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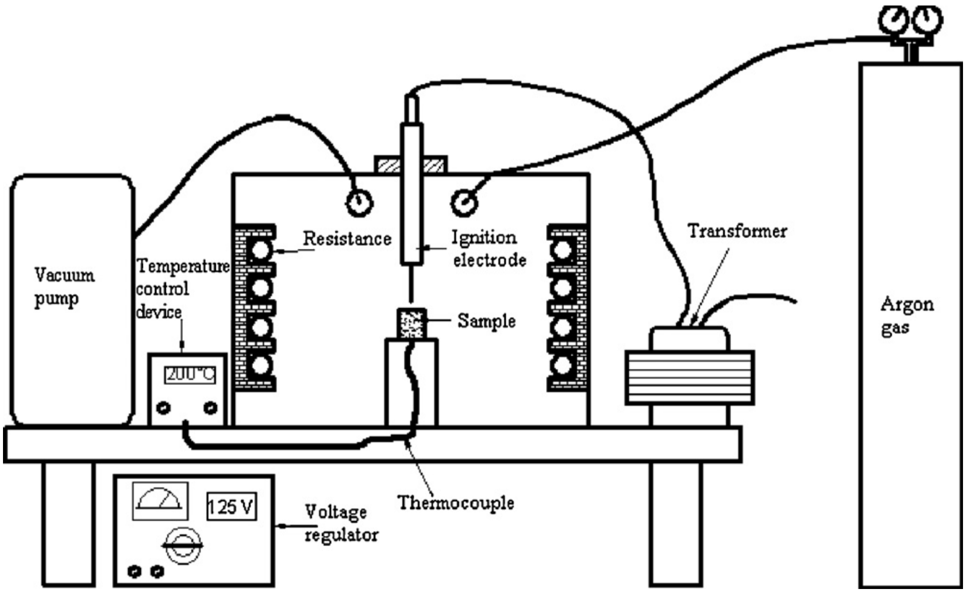


Fig. 1. Experimental setup.

Table 1
Characteristics of Ti and Ni powders [11].

Feature of material	Nickel	Titanium
Purity (%)	99.8	99.5
Specific gravity (g/mol)	58.71	47.9
Powder dimension (mesh)	−325	−325
Melting temperature (°C)	1453	1680
Specific weight (g/cm^3)	8.9	4.507
Boiling temperature (°C)	2832	3260

The general porosity of NiTi products was calculated by the following formulae:

$$\varepsilon = \left(1 - \frac{\rho}{\rho_0}\right) \times 100 \quad (1)$$

where ρ and ρ_0 are the density of the specimen and its corresponding theoretical density, respectively. The density of the specimen was determined by measuring its weight and dimension. The theoretical density of Ti–50.5 at.% Ni alloy is 6.21 g/cm^3.

The NiTi products were etched by a mixture of 10% HF, 5% HNO_3 in water after polishing [12]. The microstructure and the pore characteristics of the NiTi specimens were analyzed with optical microscope and the scanning electron microscope (SEM, LEO Evo-40VP). The chemical composition of the phases was determined by energy dispersive spectroscopy (EDS) coupled with the SEM.

3. Results and discussion

Even though the SHS technique successfully produces NiTi with the prosthesis-quality porous structure, these products are never single phase. The as-reacted porous NiTi alloy always contains other phases like $NiTi_2$, Ni_3Ti, Ni_4Ti_3 or in some cases even elemental Ni in varying proportions. Full austenitic NiTi material generally has suitable properties for surgical implantation and superelasticty. Therefore, other undesirable phases need to be eliminated. In a recent work [13], porous NiTi with adjustable porosity and size were successfully fabricated by SHS and single phase austenitic NiTi was also obtained by solution treatment under load. But solution treatment decreased porosity. The treatment should be done without reducing porosity so that ingrowth of the bone tissue is not affected. Normally, the product shows single phase microstructure when the combustion temperature or the sintering temperature is sufficiently high. But, that usually leads to melting of the product and in turn loss of porosity. So, to achieve complete conversion to the single phase NiTi and maintain its porosity too remains a challenging task. Interestingly, this aspect too has received little attention in the literature so far [7].

3.1. Effect of heating rate

From SEM and optical micrographs and EDX analyses (Figs. 2 and 3), it can be seen that the amount of NiTi phase increases with increasing heating rate [3]. Generally, the main phase microstructure in the samples heated at low heating rate (30 °C/min) is NiTi. But, these porous products contained $NiTi_2$ phase apart from the major phase, NiTi. Other binary phases could not be avoided except at higher temperature of combustion and at the expense of the product shape and porosity. In the micrographs of the specimens, NiTi matrix was seen grey, Ni_3Ti_2 or Ni_4Ti_3 phases were seen as light grey and $NiTi_2$ phase was seen as cornered shape in dark grey.

In order to maintain the integrity of the porous skeletal structure during synthesis, the rate of generation of liquid should be equal to the rate of consumption of the liquid. Therefore, the heating rate is to be proportionate with this requirement. This heating rate is defined as the threshold heating rate for melting. It was determined that threshold-heating rate was 60 °C/min in this study (Fig. 4).

The porous NiTi was obtained by keeping the heating rate below the threshold rate. When the heating rates were kept low (30 °C/min), the absorption rate of liquid could match the liquid generation rate. Thus, the low heating rate could achieve the chemical homogenization and retention of the porous structure at the same time [7].

In the samples fabricated by the heating rate of 60 °C/min, NiTi phase quantity increased whereas $NiTi_2$ phase decreased. Moreover, Ni_3Ti_2 phase also formed.

When the heating rate is low, the time needed for synthesis gets longer. Faster rates of heating increased the rate of liquid generation beyond the absorption limit, as a result of which the pores started collapsing [7].

The samples at the higher heating rates (90 °C/min) underwent melting and resulted in the loss of both the shape and the porosity. In this case, NiTi phase quantity much more increased in the samples at the higher heating rate and $NiTi_2$ phase vanished. Instead of $NiTi_2$ phase, Ni_3Ti_2 was seen (Fig. 3).

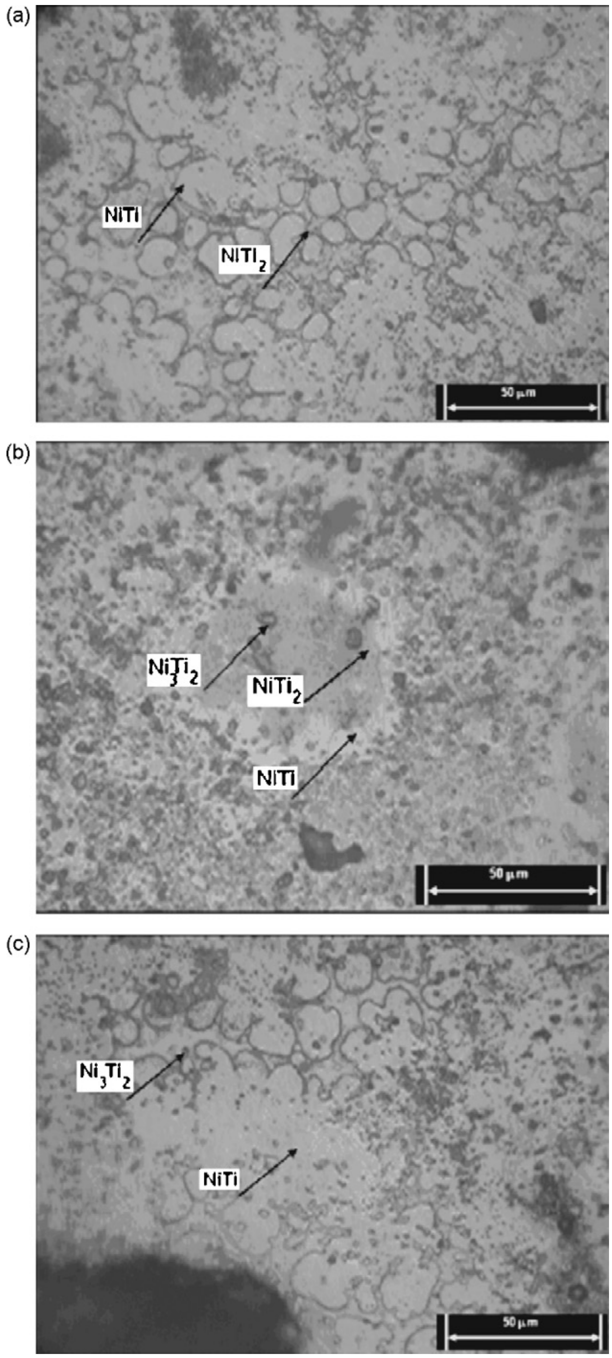
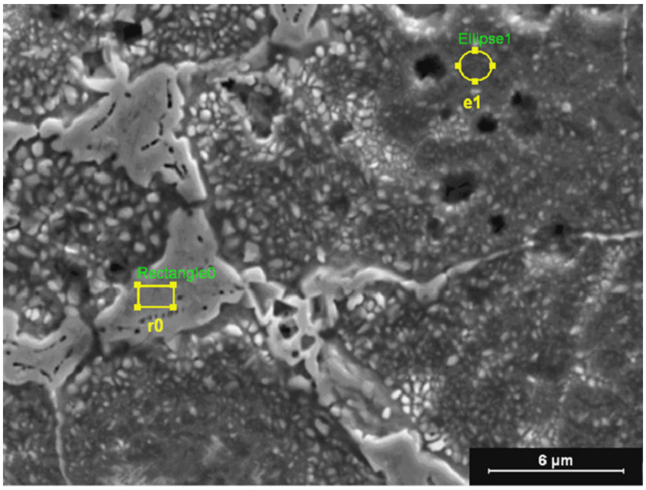
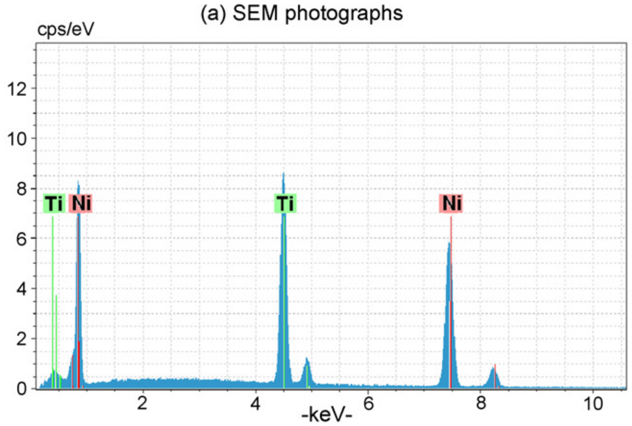


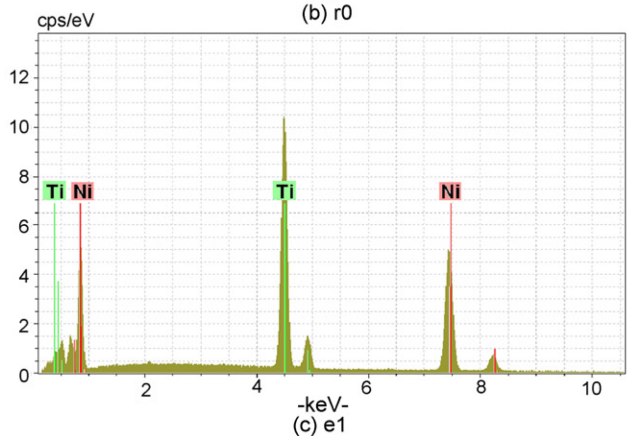
Fig. 2. Microstructure photographs of NiTi alloys produced at 100 MPa pressure, 250 °C preheating temperature and three different heating rates: (a) 30 °C/min; (b) 60 °C/min; (c) 90 °C/min.



(a) SEM photographs



(b) r0



(c) e1

Fig. 3. SEM photographs and EDX analysis of NiTi alloys produced at 100 MPa pressure, 250 °C preheating temperature and 90 °C/min heating rate.

Minimum porosity was obtained at the heating rate of 30 °C/min, and maximum porosity was determined at 60 °C/min. On the contrary, minimum density was obtained at the heating rate of 60 °C/min (Fig. 4b). When heating rate was more increased up to 90 °C/min, it can be seen that porosity decreased again (Fig. 4a).

3.2. *Effect of cold compaction pressure*

SEM and EDX analyses were performed to determine the influence of green density on the microstructure (Figs. 5 and 6). Previous experimental observations indicated that the combustion characteristics associated with the formation of NiTi intermetallics by SHS depend on both the initial sample density and the preheating temperature [3]. In the specimens with low green density (50 MPa cold compaction pressure) the main phase was NiTi and secondary phases such as $NiTi_2$ and Ni_3Ti_2 were also seen (Figs. 5 and 6). When the cold compaction pressure or green density was increased, the amount of NiTi phase also increased. The quantity of secondary phases decreased but small amount of Ni_3Ti_2 phase was observed.

Fig. 7a shows variation of porosity with pressure. It can be seen that porosity decreased with increasing compacting pressure and therefore density also increased (Fig. 7b). The initial (green) density of the compacted samples was increased with the increasing com-

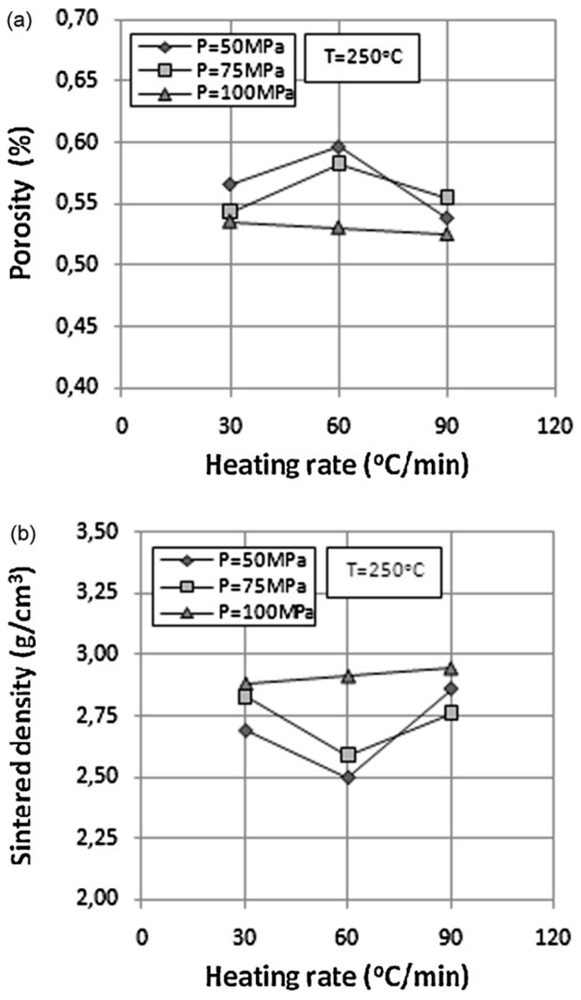


Fig. 4. (a) Porosity and (b) sintered density obtained at different heating rates.

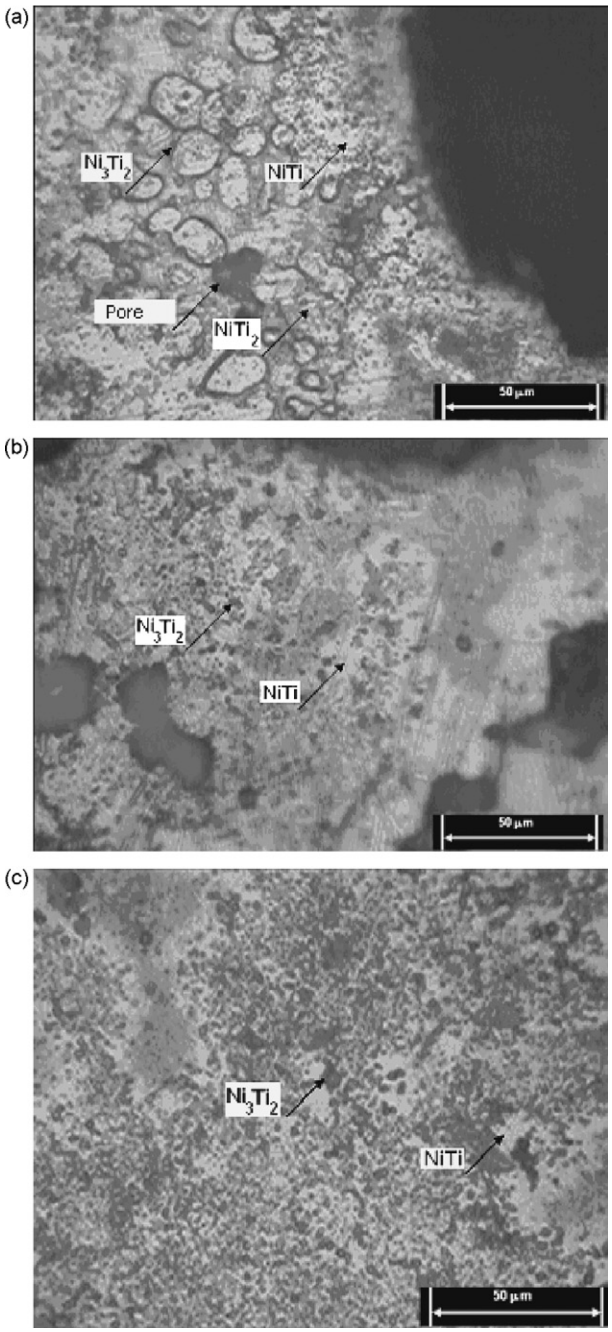


Fig. 5. Microstructure photographs of NiTi alloys produced at heating rate of 60 °C/min, preheating temperature of 250 °C and different pressures: (a) 50 MPa; (b) 75 MPa; (c) 100 MPa.

pacted pressure (Fig. 7c). Porosity in the specimens compacted by low pressure is high and its density low (Fig. 7a and b). Each pore in the structure is a barrier for the continuation of flame propagation. In other words, the synthesis is interrupted by the pores. As a result, the synthesis cannot be completed and secondary phases are present in microstructure. It indicated that not only the product composition and morphology, but also the combustion characteristics were strongly affected by the initial sample density and preheating temperature [3].

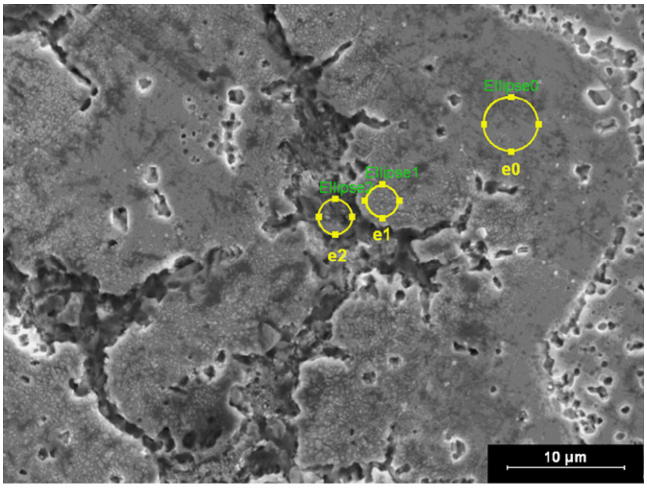
3.3. *Effect of preheating temperature*

On account of the weak exothermic heat and low combustion temperature of the Ni + Ti reaction, the combustion can only be initiated by preheating the compacts [1].

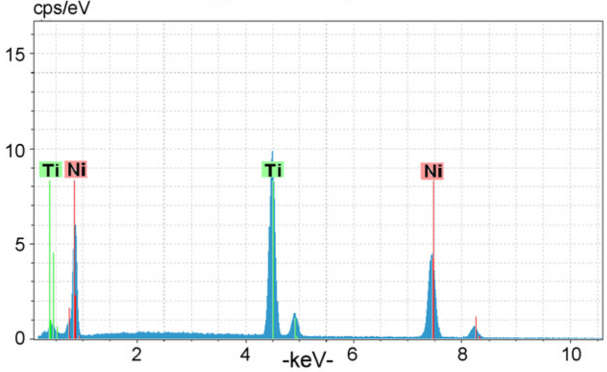
SEM and EDX analysis in Figs. 8 and 9 show the influence of the preheating temperature on the microstructure. It can be seen from the figures that the NiTi phase quantity increases with increasing preheating temperature. NiTi as the main phase and some secondary phase, $NiTi_2$, were seen in the microstructure of NiTi alloy produced at 200 °C preheating temperature. The microstructure of NiTi alloy produced at 250 °C preheating temperature consisted of NiTi main phase and secondary phases, Ni_3Ti_2 and less $NiTi_2$. The microstructure of NiTi alloy produced at 300 °C preheating temperature contained both NiTi main phase and $NiTi_2$, secondary phase.

The mechanism of SHS of porous NiTi SMAs varies with the SHS process parameters [1]. Based upon the experimental results observed, it can be concluded that SHS process can be controlled by adjusting the preheating temperature, which influences the phase amount and the macro distribution of pores in the sintered products.

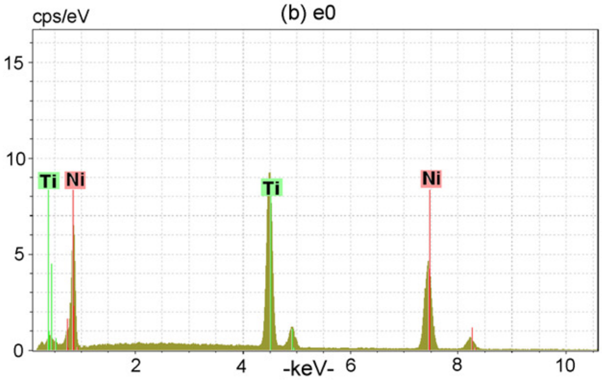
Li et al. [1] noted that the combustion does not propagate at a preheating temperature of 150 °C. Considering this, the preheating temperatures used in this study were chosen higher than 150 °C. Fig. 10a and b shows the porosity and sintered density obtained at different preheating temperatures, respectively. The sample porosity increased when the preheating temperature was increased from 200 °C to 250 °C. However, when preheating temperature was increased from 250 °C to 300 °C, porosity decreased [3].



(a) SEM photographs



(b) e0



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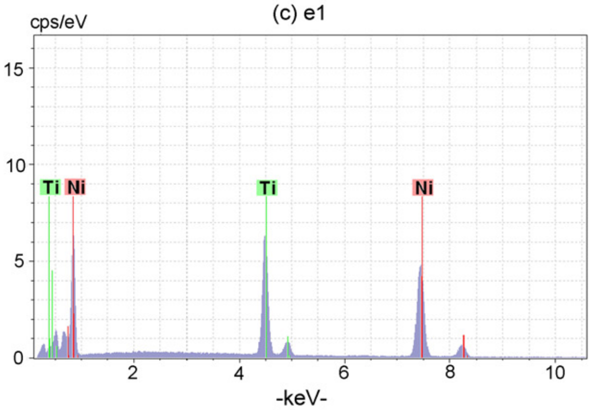


(d) e2

Fig. 6. SEM photographs and EDX analysis of produced NiTi alloys in 50 MPa pressure, 250 °C preheating temperature and 60 °C/min heating rate.

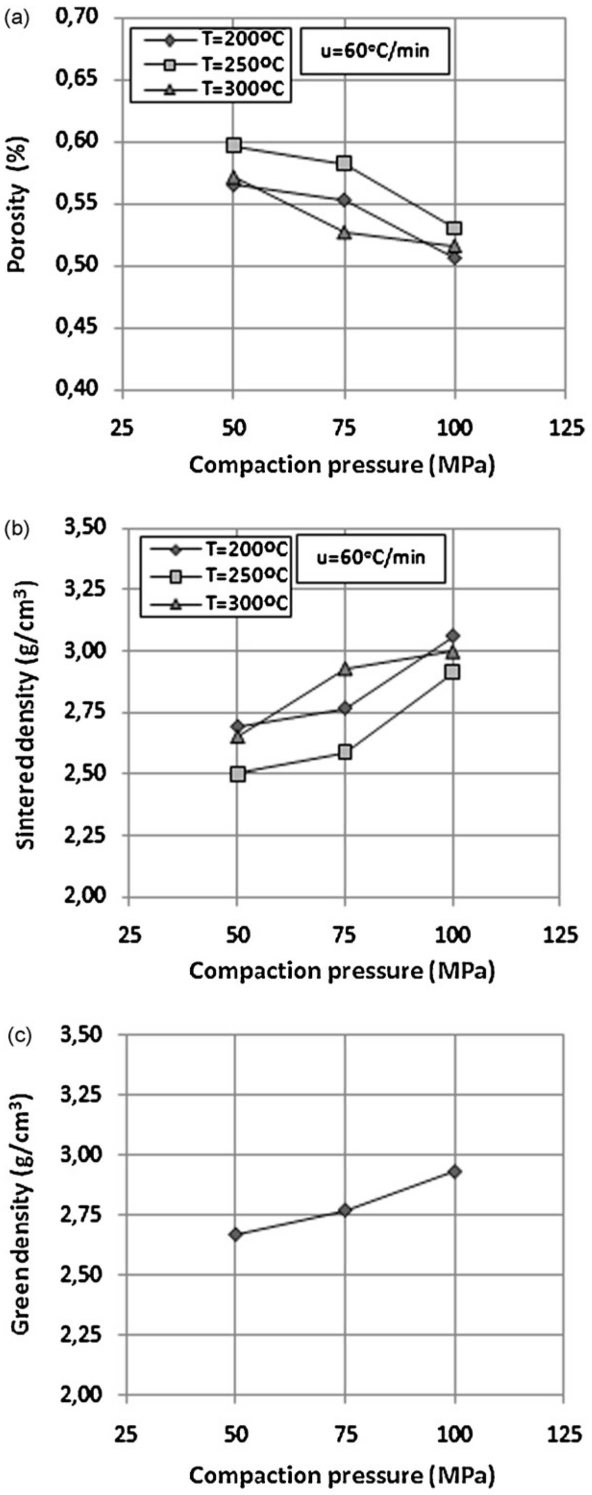


Fig. 7. (a) Porosity; (b) sintered density and (c) green density obtained at different pressures.

Even if some secondary phases appeared beside NiTi, the major phase, threshold preheating temperature is determined as 250 °C from the porosity results

4. Conclusions

This study presents a comprehensive description of the SHS process associated with the formation of NiTi intermetallic com-

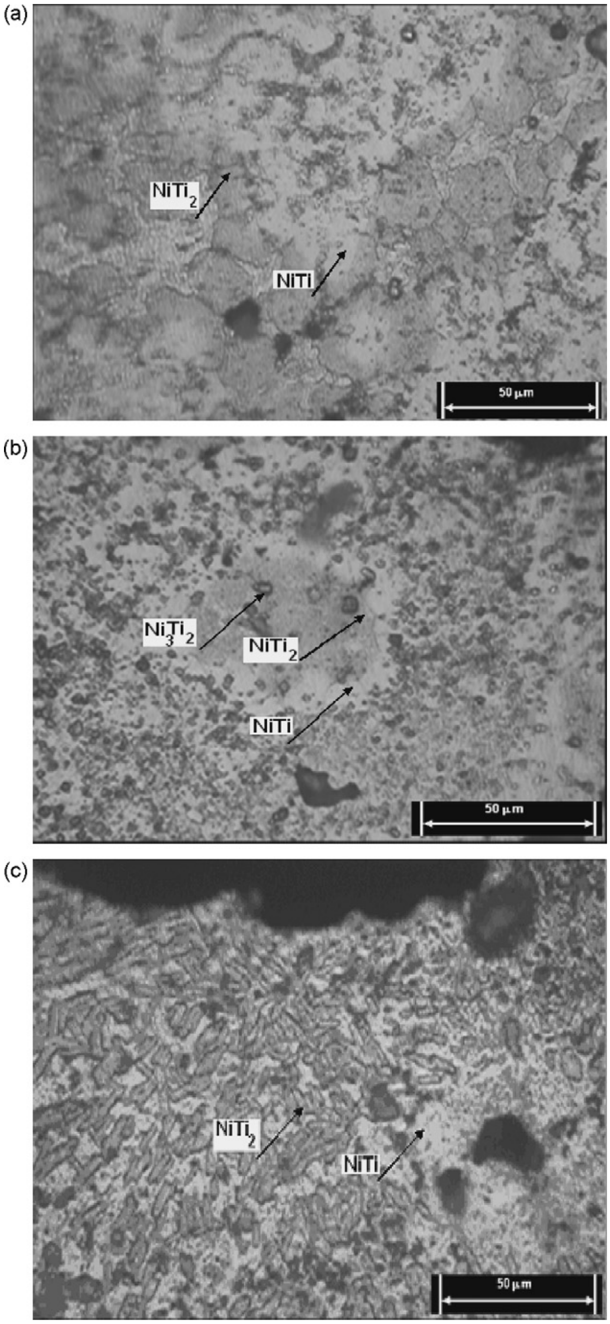
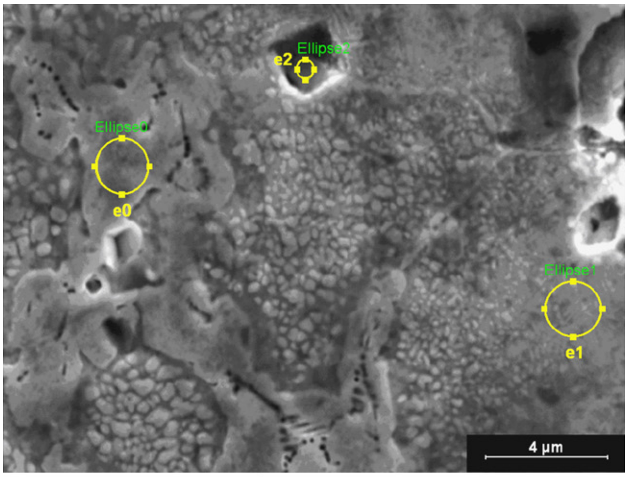


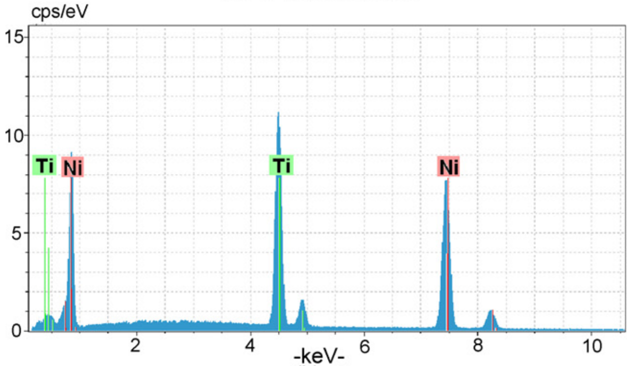
Fig. 8. Microstructure photographs of produced NiTi alloys at 60 °C/min heating rate, 100 MPa pressure and (a) 200; (b) 250; (c) 300 °C preheating temperature, respectively.

pounds from elemental powder compacts. It was found that not only the product composition and morphology, but also the combustion characteristics are strongly affected by the initial sample density, preheating temperature, and heating rate.

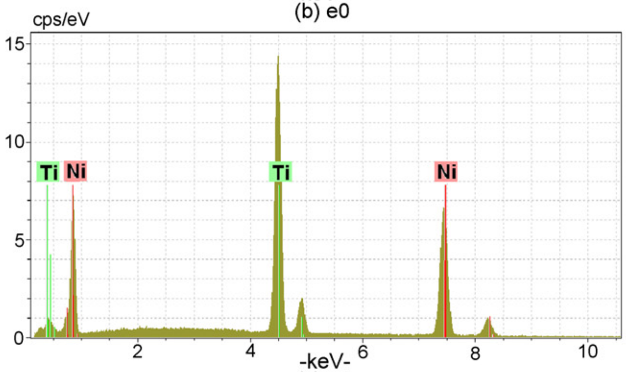
When the heating rates were kept very low (30 °C/min), the rate of absorption of liquid could match the liquid generation rate. Thus, the low rate of heating could achieve the chemical homogenization and retention of the porous structure at the same time. In microstructure of heating rates of 60 °C/min, in microstructure of samples, NiTi phase quantity increased and $NiTi_2$ phase decreased. Ni_3Ti_2 phase formed in case of threshold-heating rate was 60 °C/min in this study. However, the higher rates of heating (90 °C/min) products underwent melting and resulted in the loss of both the shape and the porosity. In microstructure of samples at of



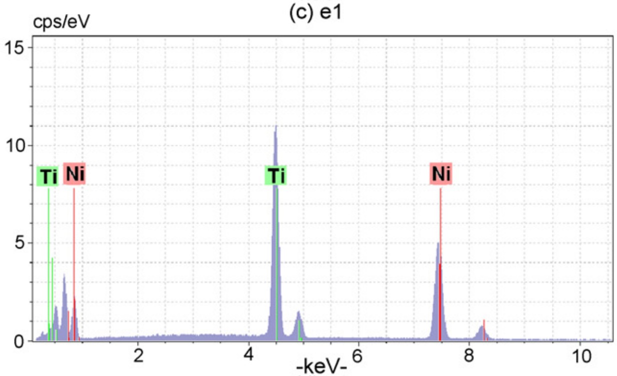
(a) SEM photograph



(b) e0



(c) e1



(d) e2

Fig. 9. SEM photograph and EDX analyses of produced NiTi alloys at 75 MPa pressure, 250 °C preheating temperature and 60 °C/min heating rate.

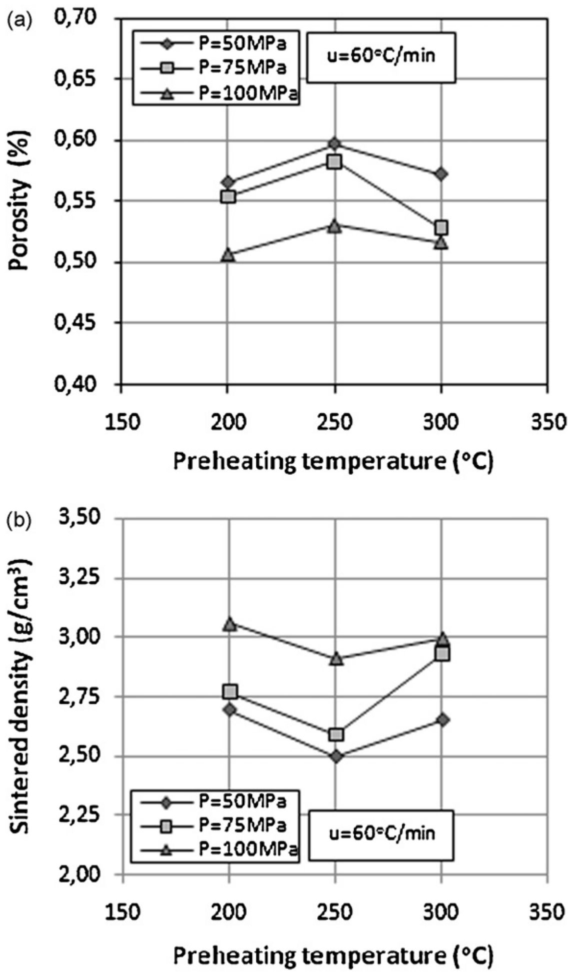


Fig. 10. (a) Porosity and (b) sintered density obtained at different preheating temperatures.

90 °C/min heating rates, NiTi phase quantity much more increased and $NiTi_2$ phase vanished but Ni_3Ti_2 phase appeared

Green density affects the phases formed. Secondary phases such as $NiTi_2$ and Ni_3Ti_2 were also seen beside the major phase NiTi when the green density was low. The increase in green density causes NiTi phase to increase, secondary phases to decrease and little amount of Ni_3Ti_2 phase to form

Preheating temperature has a considerable effect on porosity in some temperature ranges. Porosity increases and density decreases at the preheating temperatures between 200 °C to 250 °C and porosity decreases and density increases at the preheating temperatures between 250 °C and 300 °C.

Threshold heating rate is 60 °C/min for porosity.

NiTi SMA with highest porosity was obtained at a heating rate of 60 °C/min, a preheating temperature of 250 °C.

It is inevitable formation of undesirable phases such as $NiTi_2$ and Ni_3Ti_2 phases with the parameters used in this study.

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