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# Effect of Heat Treatment on Phase Transformation of NiTi Shape Memory Alloy Produced by Metal Injection Moulding

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## ABSTRACT

*The NiTi alloy is widely known for its unique properties which are pseudoelastic and shape memory effect. These two unique properties are suitable for biomedical applications such as an implant, biomedical suture etc. Various methods are available to produce NiTi such as Metal Injection Molding (MIM), Vacuum Arc Melting (VAM), Additive Manufacturing (AM), etc. The most common method is MIM, where the specimen undergoes the process of mixing, injection moulding, debinding and sintering. Commonly after the sintering process, the sample is inhomogeneous due to the formation of secondary phases and impurity content. These impurities content can be reduced by applying heat treatment which improves the microstructure of NiTi. The objective of the study is to investigate the effect of heat treatment on the microstructure and phase transformation of NiTi. In this study, samples were fabricated with each 50.0at% and 50.8at% of NiTi composition by using MIM. An annealing heat treatment of 430˚C was applied to the heat-treated samples for increasing the yield strength of NiTi. All heat-treated samples were subjected to Differential Scanning Calorimetry (DSC) test for analysing the phase transformation; X-Ray Diffraction (XRD) test for identifying the existence of any secondary phases; and Scanning Electron Microscopy (SEM) test for observing the change in the microstructure. The results indicated that upon heating through the annealing process, the secondary phase of martensite, which is known as*

*NiTi (B19') diffused and formed the austenite phase of NiTi (B2). Results from the DSC and SEM analyses showed that the formation of B2 is dominant after the heat treatment process.*

***Keywords**:nickel titanium, metal injection moulding, pseudoelastic, shape memory effect*

## INTRODUCTION

Nickel Titanium (NiTi) alloy has many potential applications in the engineering industry. Due to its unique shape memory effect (SME) and pseudoelasticity (PE), it can be used as an active, adaptive, or smart structure for biomedical applications [1][2]. Generally, NiTi alloy can be manufactured by various methods such as Metal Injection Molding (MIM), Vacuum Arc Melting (VAM), Additive Manufacturing (AM), etc. MIM is widely used in the production of metallic biomaterials as it can minimize the secondary operation due to the complex shape of the implant or extensive joining samples. There are four crucial steps to the fabrication of NiTi alloy; (1) mixing, (2) injection moulding, (3) debinding, and (4) sintering [3].

The equiatomic NiTi alloy is capable of portraying SME when subjected to heat treatment [4]. Before the NiTi alloy was found, the Au-47.5at%C alloy was discovered to have a similar SME [4]. Despite the phenomena and the martensitic transformation was understood, the development of NiTi alloy did not progress rapidly. The phase diagram of the NiTi alloy system is quite complicated and has been a subject of debate until the end of 1980's. Apart from the SME and PE, NiTi alloy also has a low elastic anisotropy, quite ductile, corrosion resistance, and abrasive resistance [5]. As a result, NiTi alloy is widely used in the biomedical field, mechanical, and even aerospace industries [6]. The NiTi alloy has a high elastic limit and low elastic modulus for clinical use in clinical orthodontics [7]. The SME property of NiTi alloy changes drastically with variation in chemical composition, material processing and thermomechanical cycling [8]. A slight change in the elemental composition may impact the transformation temperature of NiTi alloy. The reversible phase transformation from austenite to martensite for NiTi alloy is very sensitive to a small variation of Ni and Ti composition [9]. The formations of intermetallic phases and

secondary phases are easily formed since the transformation temperature is susceptible to the formation of impurities [10][11]. Besides that, the decreased solubility of Ni at lower temperature leads to the formation of the finely dispersed metastable $Ni_4Ti_3$ phase [12][13].

In this study, specimens with different chemical composition and produced at heat treatment temperature were analysed to investigate the effects of heat treatment on microstructure and phase transformation of the NiTi alloy. The phase transformation temperature of the NiTi alloy was investigated using DSC tests, and the microstructure changes before and after the heat treatment process were analysed with SEM.

## METHODOLOGY

The average particle size for Ni and Ti powders are 8µm and 11µm, respectively. A composition ratio of 50.8at% Ni and 50at% Ni were used. The manufacturing route is metal injection moulding and the parameters used were reported by Razali et al. [9]. The specimen was fabricated in a dog bone shape a tensile shape cavity according to ASTM 638 type V. The binder system consisted of of palm stearin (PS) and polyethylene (PE) with fraction of 60/40 by weight fraction. After injection moulding, the specimens were then immersed in a heptane solution to remove the palm strearin binder at $60_oC$ for five hours. The specimens were sintered at temperature 1150˚C for one hour. The sintering started by heating at a ramp rate of 3°C/min from room temperature to 500°C for thermal debinding and was held for one hour. Then, the sintering process was continued until 1150˚C at a ramp rate 10˚C/min followed by an hour of holding time. The furnace was allowed to cool at a natural rate with no power supplied. The heat treatment of the NiTi alloy samples was conducted according to Yan et al. [13]. The transformation strain of specimen increases at all stress levels when annealed at a lower temperature (i.e., 350-450˚C) and decreases when annealed at a higher temperature (i.e., 550-650˚C) [13]. Thus, the annealing process was conducted at 430˚C for 15 minutes. A heating rate of 5˚C/min was chosen as it has proven to exhibits difference in strain between heat-treated and non-heat treated specimen [14]. Then, the heated samples were analysed with a differential scanning calorimetry (DSC) using method ASTM F2004 for analysing the transformation temperatures. The samples were heated at

a rate of 10 ˚C/min under nitrogen cover gas. Two DSC cycles were done ranging from -60 to 170 ˚C, performed consecutively for each sample, and the second cycle was used to determine the transformation enthalpy and the phase-transformation temperatures [15]. To identify the phase and composition presents, X-ray diffraction was conducted using a wavelength of 1.540562Å with a diffraction angle from 30˚ to 90˚ at scanning speed of 1˚/min. Finally, for microstructure observation, the specimens were analysed using a scanning electron microscope (SEM). In this test, the Hitachi TM3000 was used to evaluate the microstructural changes as a function of heat treatment.

## RESULT AND DISCUSSION

### Phase Evaluation by XRD Analysis

Figure 1 (a) and (b) show the XRD spectra of untreated and heat-treated NiTi alloy. It shows different phase changes as a result of heat treatment of the equiatomic NiTi alloy. Figure 1(a) shows the presence of secondary phase known as Ni4Ti3 in the as-sintered samples of MIM 50.0at% NiTi . The formation of this phase occured during the slow cooling of NiTi alloy during the MIM procedure. However, upon heating through the annealing process, this phase maintained its state which resulted in the R-phase formation. The martensite phase of NiTi (B19') diffused and formed the austenite phase of NiTi (B2) upon heating. The austenite peak is located between 42˚ to 45˚. From the binary Ni-Ti phase diagram, NiTi, $NiTi_2$ and $Ni_2Ti$ are stable phases. The secondary phases are more thermodynamically favourarable than NiTi as the amount of energy was exerted during the formation of phases. Thus, it is difficult to completely remove secondary phases from the NiTi alloy only by altering heat treatment [16].

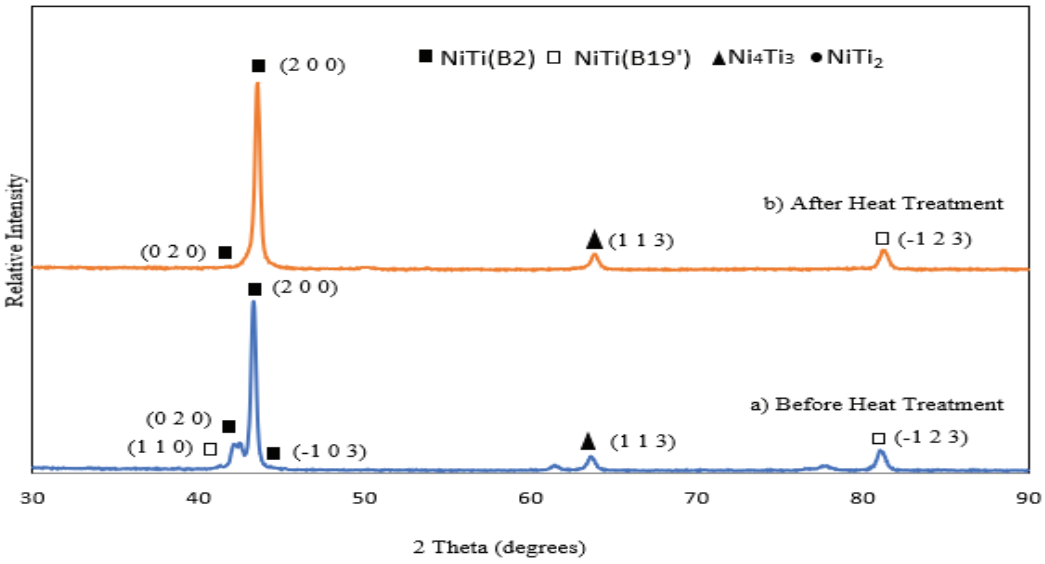


**Figure 1(a): XRD Pattern of MIM 50.0at% NiTi**

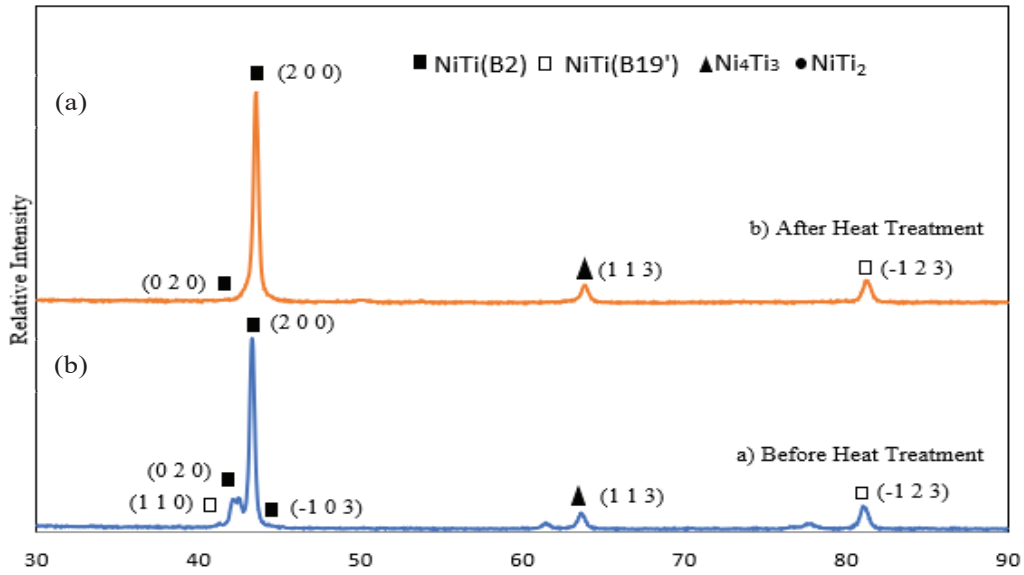


**Figure 1(b): XRD Pattern of MIM 50.8at% NiTi**

## Microstructure Evaluation by SEM

Further investigation was carried out to confirm the phase identified using the SEM analysis. The images of the microstructure were recorded at 80x and 500x magnification. As shown in figure 2(a) and (b), all samples between 50.0at% and 50.8at% showed identical microstructure. The specimen produced by MIM technique shows a significant change in the pore development as the pores are interconnected to each other and larger

than that of the as-sintered specimen. The formation of large interconnected pores may be due to the Kirkendall effect [17]. The large pores in NiTi alloy may be due to the entrapment of air in the moulding process during fabrication stage, leading to gradient powder packing in the sample [18]. The different grey scales in Figure 2 illustrated that different phases may have existed. The darkest side indicated lower atomic mass and the lightest side illustrated higher atomic mass. The Ni-rich phase, particularly $Ni_4Ti_3$ with higher atomic mass, was observed as the brightest grey-scale contrast and Ti-rich phase such as $NiTi_2$ was observed as darkest grey-scale contrast. The dark grey region is proven to be the titanium rich phase ($Ti_2Ni$) as proven through the XRD analysis (Figure 1).

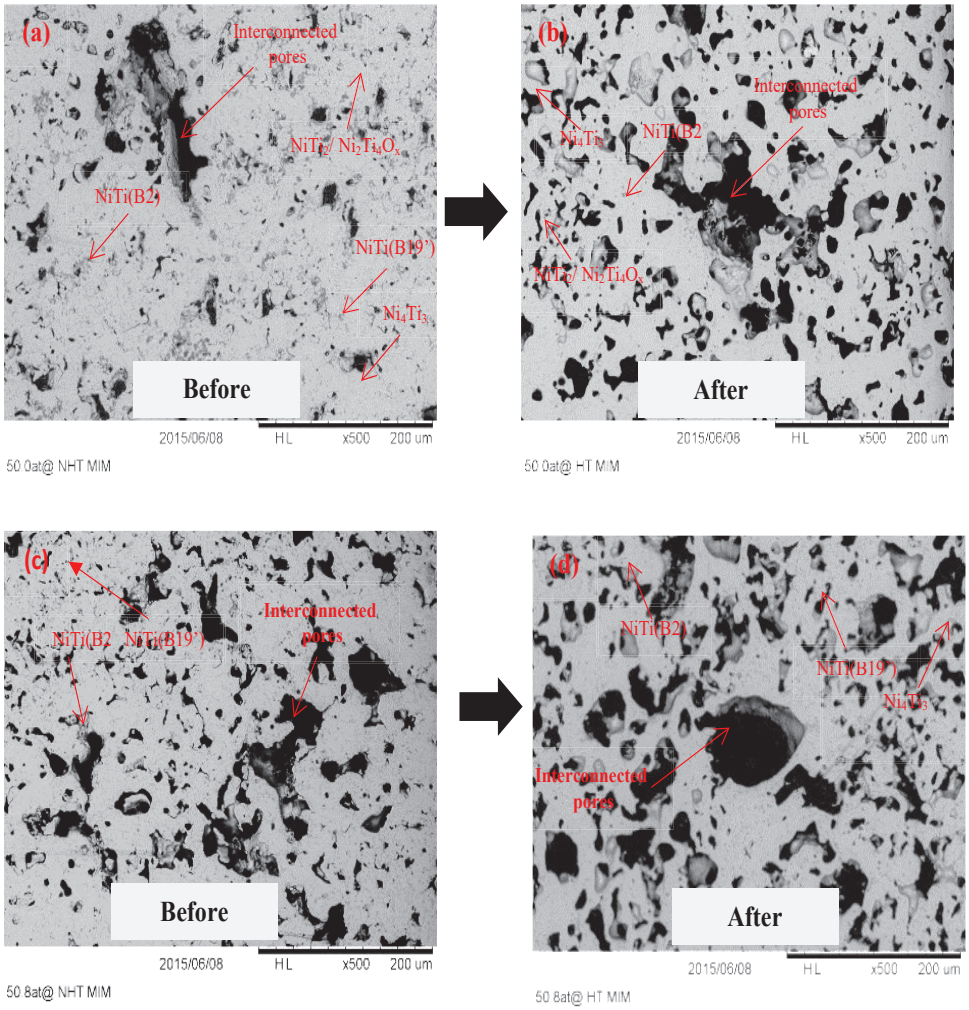


**Figure 2: SEM for Specimen Before Heat Treatment and After Heat Treatment (a) 50.0 at% NiTi Before Heat Treatment (b) 50.0 at% NiTi After Heat Treatment and (c) 50.8 at% NiTi Before Heat Treatment and (c) 50.8 at% NiTi After Heat Treatment**

The phase diagram for NiTi is shown in Figure 3. The $Ti_2Ni$ phase is thermodynamically stable above the sintering temperature of the MIM samples (i.e., 1150˚C). These lines are the martensite (B19') phase which exists during the sample preparation for metallographic evaluation of austenitic (B2) NiTi shape memory alloy. This corroborated with the presence the B19' and B2 phase of NiTi transformation in the XRD spectra (Figure 1). The $Ti_2Ni$ phase can be stabilised by the oxygen pick-up during the melting of NiTi even under high vacuum condition [19].

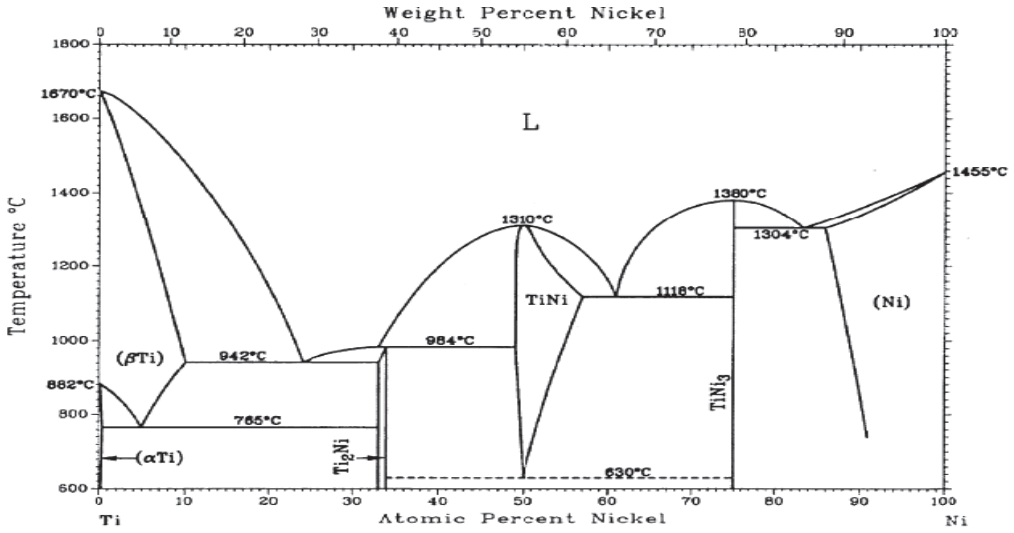


**Figure 3: Binary Phase Diagram of NiTi Alloy [20]**

## DSC Analysis

Figure 4(a) and (b) show the DSC thermograms of the as-sintered specimens and after heat treatment process. It showed that all samples exhibited reversible phase transformation which indicated the formation of martensitic structure (B19') to austenitic phase (B2) temperature. Overall, the enthalpy changes for the heating and cooling transformations between martensite and austenite are greater than those for the as-received samples. Figure 4(a) shows the DSC curve difference between the as-sintered and as-heat treated samples at 430˚C with MIM 50.0at% NiTi. The figure shows a distinct difference between the two samples in which the heat-treated sample shows clear peak of the austenite and martensite phases. The heat treatment increased the Af. After heating at 430˚C, a small peak of two-step transformation upon cooling and a one-step transformation upon heating had taken place. The two-step transformation is the transition between the

B2/R-phase to R-phase/BA19'. Both composition of 50.0at% and Ni-rich NiTi produced by MIM shows the same pattern of phase transformation. In Figure 4(a), the transformation of austenite during heating began at -30.16 ˚C and ended at 40.5˚C. There is the R-phase occurrence during the cooling process which peaked at 68.66˚C. Meanwhile, the martensitic transformation of the sample occurred between 33.33˚C and -37.33˚C. The formation of the R-phase as the first peak during cooling was due to the low energy requirement to form the $Ni_4Ti_3$. This precipitate exists as the result of a slow cooling rate [19].

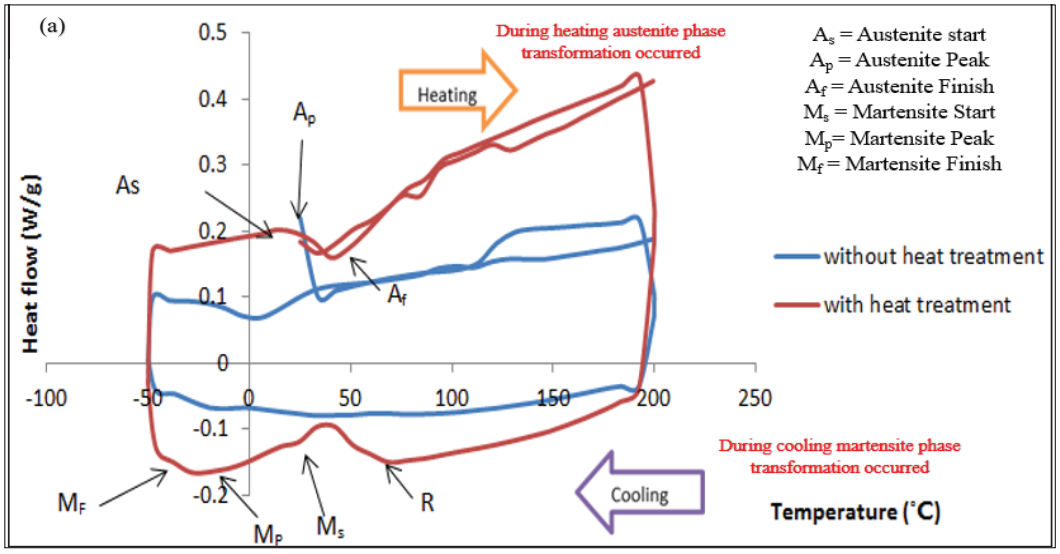


**Figure 4 (a): DSC Curve for MIM with Composition of 50.0at% NiTi**

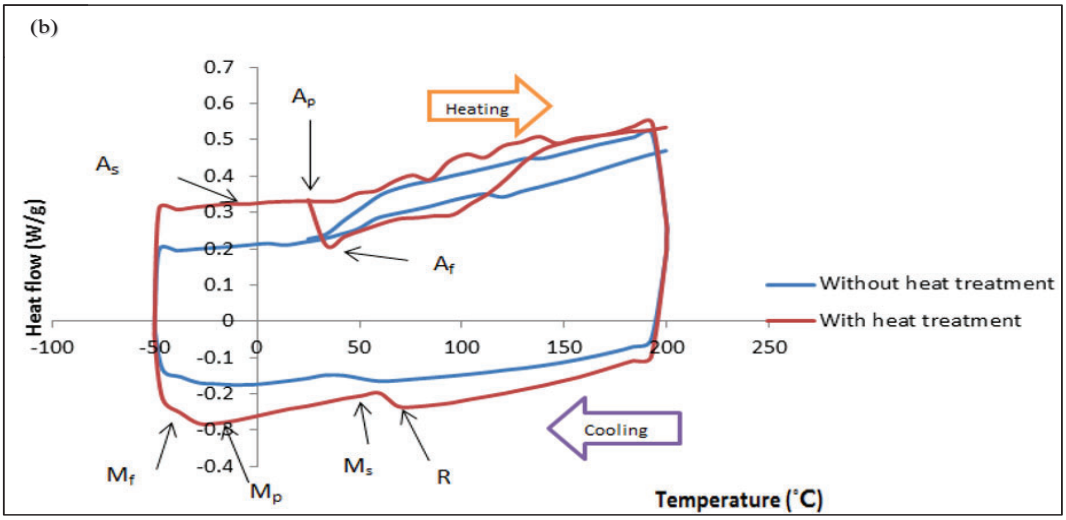


**Figure 4 (b): DSC Curve for Composition of 50.8at% NiT**

Figure 4 (b) shows the same process of MIM samples with Ni-rich composition of 50.8at%NiTi. The DSC curves for both composition of NiTi are similar. The transformation of austenite during heating began at -39˚C and ended at 35.67 ˚C. The R-phase also occurred in the cooling process. Two peaks were detected with the highest peak at 77.5˚C. The peak observed at between 33.33˚C and -37.33˚C in DSC thermogram shows that the martensite phase transformation of the sample has occured. The existence of $Ni_4Ti_3$ before and after the heat treatment causes the formation of R-phase. R-phase usually found during cooling or heating process, whereby, R-phase intervenes between austenite and martensite on both heating and cooling. This can be identified where two peaks were observed during the cooling and heating process, and the peaks are much closer to one another due to the lower hysteresis of the A-R transformation. This is proven based on the identification of secondary phase in the XRD spctra. The MIM technique affect the impurity content of the samples due to oxygen impurities created during the fabrication process. The Ti-rich impurity phases (TiC or $TiO_2$) appeared in the binary NiTi matrix that has changed the composition in favour of an Ni-rich phase, resulting in the phase transformation properties shift compared to the initial alloyed NiTi powders [20]. As shown in the XRD and SEM analyses, the excessive remelting processes has caused pick-up of oxygen and carbon, thus, reducing the homogeneity and caused the formation of secondary phases such as $Ti_4Ni_2O$ and TiC. The specimen shows a one-step phase transformation during heating where it transformed from B2 to B19'. Upon cooling, it transformed in two-step by B2/R-phase to R-phase/BA9'. This transformation is possible as the result of inhomogenities of NiTi evolves during aging and the difference between the nucleation barriers for R-phase and B19'[21].

## CONCLUSION

Heat treatment process of annealing at 430˚C has enhanced the SME and PE behaviour of NiTi as the content of the secondary phases were reduced effectively. The content of Ni-rich phase was decreased after the heat treatment. The heat treatment process caused the B19' martensite to transform to B2 austenite. Results from the DSC, XRD and SEM analyses has shown that major fraction of B2 phase (austenite) existed, while the DSC result showed the transformation peak of reversible transformation

of austenite to martensite. From the SEM analysis, the porous structure of NiTi indicated the inter-connected pores and is suitable for bone tissue growth in implants. From this work, it was found NiTi with less formation of secondary phases are suitable in medical devices where its unique properties allow for the operational of NiTi devices and implants, particularly for biomedical applications.

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## REFERENCES

[1] A. Bansiddhi, T. D. Sargeant, S. I. Stupp, and D. C. Dunand, 2008. Porous NiTi for bone implants: A review. *Acta Biomater., 4*(4), pp. 773–782. DOI: 10.1016/j.actbio.2008.02.009.

[2] N. Sabahi, W. Chen, C. H. Wang, J. J. Kruzic, and X. Li, 2020. A review on additive manufacturing of shape-memory materials for biomedical applications. *JOM, 72*(3), pp. 1229–1253. DOI: 10.1007/s11837-020-04013-x.

[3] M. H. Ismail, N. Muhamad, A. Jumahat, I. Subuki, and M. A. Omar, 2008. Study on stability of a novel binder system based on palm stearin in metal injection moulding application. *Sci. Res. J., 4*(2), p. 1. DOI: 10.24191/srj.v4i2.5655.

[4] W. J. Buehler, J. V. Gilfrich, and R. C. Wiley, 1963. Effect of low-temperature phase changes on the mechanical properties of alloys near composition TiNi. *J. Appl. Phys., 34*(5), pp. 1475–1477. DOI: 10.1063/1.1729603.

[5] K. Otsuka and X. Ren, 2005. Physical metallurgy of Ti-Ni-based shape memory alloys. *Progress in Materials Science, 50*(5), pp. 511–678. DOI: 10.1016/j.pmatsci.2004.10.001.

[6] D. Kapoor, 2017. Nitinol for medical applications: A brief introduction to the properties and processing of nickel titanium shape memory alloys and their use in stents. *Johnson Matthey Technology Review, 61*(1), pp. 66–76, DOI: 10.1595/205651317X694524.

[7] G. F. Andreasen and T. B. Hilleman, 1971. An evaluation of 55 cobalt substituted Nitinol wire for use in orthodontics. *J. Am. Dent. Assoc., 82*(6), pp. 1373–1375. DOI: 10.14219/jada.archive.1971.0209.

[8] D. A. Miller and D. C. Lagoudas, 2001. Influence of cold work and heat treatment on the shape memory effect and plastic development of NiTi. *Mater. Sci. Eng. A, 308*(1–2), pp. 161–175. DOI: 10.1016/S0921-5093(00)01982-1.

[9] R. Razali, Z. Abdullah, I. Subuki, N. Muhamad, and M. H. Ismail, 2015. The influence of NI-TI ratio on the reversible austenite-martensite transformation and mechanical properties produced by metal injection moulding. *J. Teknol., 76*(10), 75-83. DOI: 10.11113/jt.v76.5799

[10] M. Bram, M. Bitzer, H. P. Buchkremer, and D. Stöver, 2012. Reproducibility study of NiTi parts made by metal injection molding. *J. Mater. Eng. Perform., 21*(12), pp. 2701–2712. DOI: 10.1007/s11665-012-0264-6.

[11] J. Laeng, Z. Wu, Y. Wang, Y. Liu, and H. Yang, 2018. Phase Formation in Ti–Ni Binary System during Solid-State Synthesis. *Shape Mem. Superelasticity, 4(*3), pp. 351–359, DOI: 10.1007/s40830-018-0181-0.

[12] M. Bram, M. Bram, A. Ahmad-khanlou, H. P. Buchkremer, and D. Stöver, "Powder metallurgy of niTi-Alloys with Defined Shape Memory Properties," 15th Int. Plansee Semin., vol. 1, pp. 435–448, 2001.

[13] X. Yan and J. Van Humbeeck, 2011. Effect of annealing on strain-temperature response under constant tensile stress in cold-worked NiTi thin wire. Smart Mater. Res., pp. 1–6, 2011. DOI: 10.1155/2011/160927.

[14] G. Machado, H. Louche, T. Alonso, and D. Favier, 2015. Superelastic cellular NiTi tube-based materials: Fabrication, experiments and modeling. *Mater. Des., 65*, pp. 212–220,. DOI: 10.1016/j.matdes.2014.09.007.

[15] R. A. Abdul Kadir, 2017. "TiH2 microporous replication pseudo-elastic NiTi alloy by metal injection moulding / Ros Atikah Abdul Kadir. Unpublished Master dissertation, Universiti Teknologi MARA, Malaysia.

[16] M. Kaya, N. Orhan, B. Kurt, and T. I. Khan, The effect of solution treatment under loading on the microstructure and phase transformation behavior of porous NiTi shape memory alloy fabricated by SHS. *J. Alloys Compd., 475*(1–2), pp. 378–382, May 2009. DOI: 10.1016/j.jallcom.2008.07.023.

[17] M. H. Ismail, 2012. Porous NiTi alloy by metal injection moulding (MIM) using partly water soluble binder system. Available on https://ethos.bl.uk/OrderDetails.do? uk.bl.ethos.577639

[18] J. Frenzel, E. P. George, A. Dlouhy, C. Somsen, M. F. X. Wagner, and G. Eggeler, 2010. Influence of Ni on martensitic phase transformations in NiTi shape memory alloys. *Acta Mater., 58*(9), pp. 3444–3458. DOI: 10.1016/j.actamat.2010.02.019.

[19] X. Wang, B. Verlinden, and J. Van Humbeeck, 2015. Effect of post-deformation annealing on the R-phase transformation temperatures in NiTi shape memory alloys. *Intermetallics, 62*, pp. 43–49. DOI: 10.1016/j.intermet.2015.03.006.

[20] M. H. Elahinia, M. Hashemi, M. Tabesh, and S. B. Bhaduri, 2012. Manufacturing and processing of NiTi implants: A review," *Prog. Mater. Sci., 57*(5), pp. 911–94. DOI: 10.1016/j.pmatsci.2011.11.001.

[21] J. Khalil-Allafi, A. Dlouhy, and G. Eggeler, 2002. Ni4Ti3-precipitation during aging of NiTi shape memory alloys and its influence on martensitic phase transformations. *Acta Mater., 5*0(17), pp. 4255–4274. DOI: 10.1016/S1359-6454(02)00257-4.