

## Phase Transformation Temperatures (PPTs) and Microstructure of Moulded NiTi Alloy Using a Water Soluble Binder System

(Suhu Perubahan Fasa dan Mikrostruktur Aloji NiTi Teracuan Menggunakan Sistem Bahan Pengikat Larut Air)

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### ABSTRACT

*In this work, the effects of backbone polymer in the binder system mixed with pre-alloyed NiTi powder, on impurity contents, phase transformation temperatures and microstructures were investigated. A spherical gas-atomised pre-alloyed NiTi powder (50.3 at. %Ni) with a mean particle size of less than 22 µm and powder loading of 69.5 vol. % was used. The binder consisted of a water soluble binder system, mainly polyethylene glycol (PEG), with two different backbone binders, namely polyethylene 520 (PE 520) and poly-methyl- methacrylate (PMMA). The latter was used in the form of a powder and as an emulsion. Green parts were prepared by warm-press the feedstock into a cylindrical shape. The samples were then leached in warm water, thermally debound in Argon and finally, vacuum sintered at 1240°C for 10 h. The experimental results indicate that the oxygen content in the as-sintered condition increased to almost double than that of the powder state (from 0.08 to 0.14 - 0.16 wt. %) and the carbon increased by one third to half (from 0.06 to 0.08 - 0.09 wt. %). This consequently resulted in a shift of the phase transformation temperature to lower values and consequently broadened the reversible austenite to martensite transformation. The uptake of oxygen and carbon during the process led to the formation of the well-known  $Ti_4Ni_2O_x$  and TiC precipitate phases which were evident from grey-scale images of back-scattered SEM.*

*Keywords: Metal injection moulding (MIM); NiTi alloy; phase transformation temperatures (PTTs); pseudo-elasticity; shape memory*

### ABSTRAK

*Dalam kajian ini, kesan polimer sekunder di dalam campuran bahan suapan pengacuan suntikan logam yang terdiri daripada serbuk logam pra-aloi NiTi terhadap kandungan bendasing, suhu penjelmaan fasa dan mikrostruktur yang terbentuk telah dikaji. Serbuk logam NiTi yang digunakan mempunyai komposisi kimia 50.3 at. %Ni dengan saiz purata serbuk kurang daripada 22 µm dan telah dihasilkan secara pemptiran gas. Sebanyak 3 formulasi bahan suapan telah dikaji dengan menggunakan isi padu serbuk yang sama (69.5 vol. %). Komposisi bahan pengikat dalam bahan suapan adalah terdiri daripada polimer primer yang sama iaitu poli-etilena-glikol (PEG) dan polimer sekunder pula terdiri daripada polietilena (PE 520) dan poli-metil-meta-akrilik (PMMA). Untuk kes PMMA, 2 bentuk telah digunakan, iaitu pertamanya dalam bentuk serbuk dan keduanya dalam bentuk emulsi. Bahan suapan yang dihasilkan seterusnya diproses menjadi bentuk silinder dengan menggunakan kaedah padatan hangat. Sampel kemudiannya direndam di dalam air yang hangat untuk mengeluarkan bahan pengikat primer, iaitu PEG. Sampel kemudiannya dikeringkan sebelum dibawa ke relau vakum untuk proses penyahikatan terma dan persinteran. Proses penyahikatan terma dijalankan dalam persekitaran Argon dan diakhiri dengan persinteran dalam vakum pada suhu 1240°C selama 10 jam. Hasil uji kaji menunjukkan kandungan oksigen dalam sampel yang disinter meningkat hampir dua kali ganda berbanding dalam keadaan serbuk (daripada 0.08 ke 0.14-0.16 wt. %), manakala kandungan karbon pula meningkat antara separuh ke satu pertiga (daripada 0.06 ke 0.08-0.09 wt. %). Keadaan ini seterusnya menyebabkan pengurangan pada suhu penjelmaan fasa dan meluaskan julat perubahan suhu boleh balik daripada fasa austenite ke martensite. Peningkatan kandungan oksigen dan karbon pada sampel tersinter juga menunjukkan wujudnya fasa sekunder seperti  $Ti_4Ni_2O_x$  dan TiC yang dibuktikan daripada perbezaan warna pada setiap fasa pada gambarajah SEM dan seterusnya melalui bacaan EDX.*

*Kata kunci: Aloji NiTi; memori bentuk; pengacuan suntikan logam; pseudo-keanjalan; suhu penjelmaan fasa*

### INTRODUCTION

NiTi alloys are among the shape memory alloys that are widely used in industry in recent years as functional materials in various fields including the medical and aerospace applications. The unique properties of shape

memory effect (SME) and pseudo-elasticity (PE) have made them attractive for certain engineering applications, unlike other conventional alloys. These behaviours are strongly influenced by the reversible phase transformation temperatures (PTTs) of the austenite to martensite transition,

which is attributed to the chemical compositions, as well as the level of impurities of the alloys (Duerig et al. 1999; Yen et al. 2011).

Among the NiTi production routes, powder metallurgy (PM) technique has been proven successful and economical in producing near-net-shape components (Bram et al. 2002; Mentz et al. 2006, 2008; Yen et al. 2011). In particular, metal injection moulding (MIM) has been successfully exploited for production both porous and bulk NiTi alloys (Bram et al. 2002; Imgrund et al. 2008; Ismail et al. 2012; Köhl et al. 2009; Krone et al. 2005; Mentz et al. 2006, 2008; Schüller et al. 2005). One of the greatest challenges in the manufacture of NiTi components by MIM is the adequate control of impurities such as oxygen, carbon and nitrogen arising from the binder systems used in the process which are commonly comprised of wax-based and polymeric materials (Bram et al. 2002; Mentz et al. 2008). The development of a suitable binder system is one of the main tasks in shaping NiTi alloys by MIM with acceptably low levels of contaminants.

The objective of the present study was to investigate the feasibility of using the water soluble, PEG based binder system for a pre-alloyed and gas atomized NiTi powder with three different backbone polymers. The effect of these backbone polymers on impurity contents, phase transformation behaviour and microstructures are comparatively studied.

#### EXPERIMENTAL DETAILS

A pre-alloyed NiTi powder (Nanoval, Berlin Germany) with a composition of 50.3 at. % Ni and mean particle size of 15  $\mu\text{m}$ , produced by a plasma induced gas atomization (PIGA) process as shown in Figure 1, was used. The binder

comprised of a water soluble binder system, mainly polyethylene glycol (PEG), with two different backbone binders, namely polyethylene 520 (PE 520) and polymethyl metacrylate (PMMA). The latter was used in the form of a powder and as an emulsion. Stearic acid was used in all feedstocks as a lubricant to facilitate moulding process. Table 1 shows the formulation of the feedstocks used in the present study with a constant powder loading by weight ratio, PEG:PMMA/PE520:SA = 83:15:2.

Mixing was carried out manually in a rectangular shaped aluminium crucible, which was heated by a hot plate with the temperature set to just above the melting temperature of the polymers. The powder-binder mixture was mixed with a spatula for about 30 min to ensure homogeneity of the feedstock. The feedstock were cooled and then pelletized. A uni-axial warm pressing machine with a 12 mm diameter mould was used to prepare the moulded parts. All samples were prepared with a constant pressure and holding time of 900 MPa and 15 s, respectively. The green compacts were leached in distilled water at a temperature of 40°C for 24 h. They were then placed in an oven at a temperature of 50°C for 8 h to drive off any residual moisture from the parts. Thermal debinding and sintering were carried out in a single furnace using a Thermal Technology vacuum furnace. The samples were sintered at 1240°C for 10 h under a vacuum of less than  $10^{-3}$  Pa.

The characterisation of all samples was done in the as-sintered state (furnace cooled) without additional heat treatments. The density for all samples was determined by pycnometry, using Accupyc® under a flow of Helium gas. The samples were diamond cut for differential scanning calorimetry (DSC) tests (using a 2920 CE machine from TA Instruments), chemical analyses (LECO melt extraction

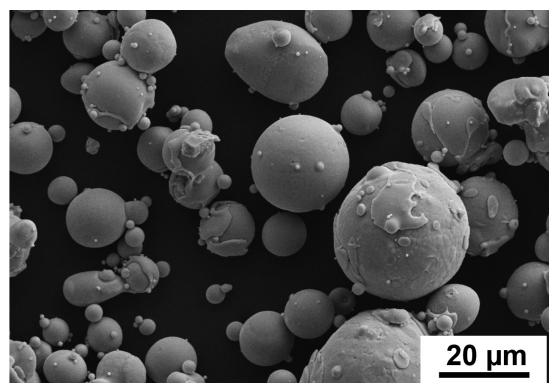


FIGURE 1. SEM micrograph of pre-alloyed NiTi powder

TABLE 1. Formulation of the feedstocks

Feedstock	Binder composition	Binder weight fraction (wt. %)
BS1	PEG/PE520/SA	83/15/2
BS2	PEG/PMMA <sub>powder</sub> /SA	83/15/2
BS3	PEG/PMMA <sub>emulsion</sub> /SA	83/15/2

system) and metallographic sample preparation. The as-sintered samples were mounted and infiltrated with epoxy resin, ground and polished. Microstructural back-scattered image analysis and elemental analysis were carried out using a scanning electron microscope (SEM) (model Zeiss Ultra 55) and energy dispersive X-ray spectroscopy (EDX) (model Inca energy 355), respectively.

## RESULTS AND DISCUSSION

Table 2 shows the impurity contents for the starting NiTi powder and the as-sintered parts produced with different backbone polymers. The impurity contents from the previous studies are also compared. It is clear that, the impurity contents for all sintered samples are higher than the starting powder, which is mainly attributed by the residuals from the organic binder materials (Bram et al. 2002). The oxygen and carbon contents for all sintered samples increase nearly double and one third to half, respectively, in comparison with the starting powder. The nitrogen contents for all samples were fairly low and comparable to the starting powder.

The lowest oxygen and carbon contents of 0.11 and 0.04 wt. %, respectively, have been reported by Mentz et al. (2006). However, this was largely resulted from the initial powder with still lower initial impurity contents; the oxygen and carbon contents for the pre-alloyed NiTi powder were 0.05 and 0.04 wt. %, respectively. It is clear that, due to impurity contained in the starting powder coupled with several steps involved in MIM, it is almost difficult to reduce the oxygen content of the as-processed parts to a minimum value. However, the carbon concentration can be reduced significantly if suitable binders can be identified and optimized process parameters are used (Köhl et al. 2009; Mentz et al. 2006). The impurity results obtained in the present work are still considerably low in comparison with other work using MIM method (Bram et al. 2002; Imgrund et al. 2008), indicating that PEG-based binder systems are an attractive proposition for MIM of NiTi alloys.

It has also been reported that a Ti-rich precipitate phase,  $\text{Ni}_2\text{Ti}_4\text{O}_x$ , which is known as brittle, tends to form in NiTi matrix if the oxygen content exceeds the solubility limit of 0.045 at% (Bram et al. 2002). It was proven by *in situ* tensile testing incorporated with scanning electron

microscope (SEM) reported by Mentz et al. (2006), in which cracks initiated in the  $\text{Ni}_2\text{Ti}_4\text{O}$  phase, an impurity phase without shape memory properties. In addition, the negative impact of higher carbon content is the restriction of the pseudoelastic regime as a result of formation of the other Ti-rich precipitate, namely TiC. As a result, the elastic modulus of the parts would be increased and the fracture strain would be lowered significantly.

Figure 2 shows the influence of different backbone polymers on the DSC thermal scan in comparison with the pre-alloyed NiTi powder. A reversible phase transformation from martensite ( $M$ ) to austenite ( $A$ ) during heating and cooling is clearly evident, attributed to the shape memory effect of the alloys. For the starting powder, the austenite formation starts ( $A_s$ ) at 37°C and finishes ( $A_f$ ) at 62°C during heating, corresponds to 25°C of austenitic transformation width, while the martensite starts ( $M_s$ ) at 27°C and finishes ( $M_f$ ) at 1°C, during cooling, corresponds to a transformation width of 26°C.

For the as-sintered samples, different ranges of transformation temperature are evident and the transformation ranges are significantly broadened, which seems to be consistent with the increased impurity contents. Samples with the lowest impurity, BS2 exhibits a better phase transformation width, 30°C from  $A_s$  to  $A_f$  during heating and 28°C from  $M_s$  to  $M_f$  during cooling. For both BS1 and BS3, the transformation temperature ranges are broadened, greater than 40°C during heating due to slightly greater amount of impurity contents as compared with BS2 samples. A similar trend as that seen for heating was observed during cooling of the as-sintered samples. It is also noticed the starting phase transformation temperature is shifted almost 25°C lower. The samples with the highest impurity content (BS3) corresponded with a shift of  $A_s$  to the lowest value measured in this study.

Study conducted by Bram et al. (2002) on MIM of pre-alloyed NiTi (50.9 at. %Ni) using a wax-based binder system showed that the high impurity contents, oxygen (0.23 wt. %) and carbon (0.14 wt. %) in the as-sintered samples resulted in strong increase of the transformation temperatures in comparison to the starting powder (approximately +80°C for  $M_p$  and +70°C for  $A_m$ ). They also concluded that besides the increased impurity, the evaporation of Ni atoms during sintering under vacuum

TABLE 2. Impurity contents of the as-sintered NiTi

Sample	Nitrogen (wt. %)	Oxygen (wt. %)	Carbon (wt. %)
Starting powder	< 0.0005	0.08	0.06
BS1	<0.0005	0.1524 ± 0.0051	0.0833 ± 0.0054
BS2	0.0010 ± 0.0002	0.1377 ± 0.0022	0.0802 ± 0.0028
BS3	0.0006 ± 0.0001	0.1643 ± 0.0092	0.0911 ± 0.0003
NiTi Powder (Bram et al. 2002)	<0.0005	0.077	0.069
As-sintered (Bram et al. 2002)	<0.01	0.23	0.14
NiTi powder (Köhl et al. 2008)		0.05	0.04
As-sintered (Köhl et al. 2008)		0.14	0.04
As-sintered (Imgrund et al. 2008)	-	0.217 -0.250	0.212 - 0.250

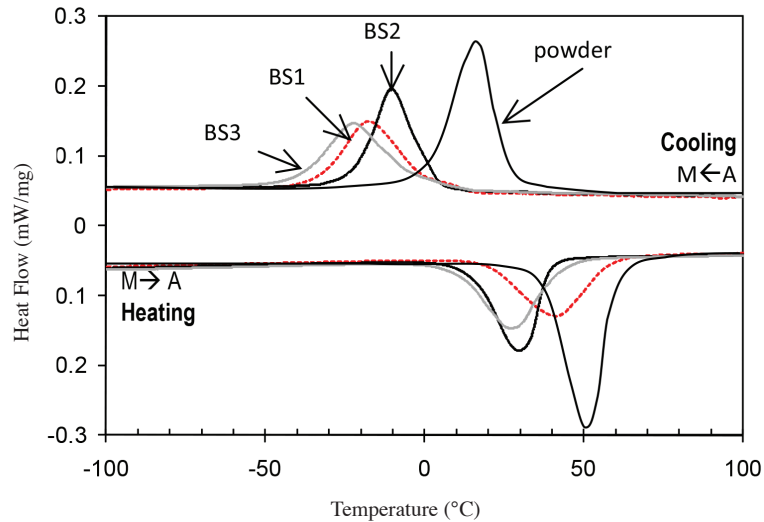


FIGURE 2. DSC traces showing PTTs of the as-sintered parts and pre-alloyed NiTi powder

and the uncontrolled precipitation of metastable phases during furnace cooling were other reasons influencing the extent of transformation temperature shift.

Figure 3 shows an example of the back-scattered SEM image for the cross section of the BS2 to confirm the phase constituent in each phase identified. The phases can be clearly distinguished by their grey scales, indicating the formation of precipitates other than NiTi after the sintering process. The SEM images show very similar well-defined phases and are as reported in previous studies using MIM methods (Bram et al. 2002; Imgrund et al. 2008; Krone et al. 2005; Mentz et al. 2006; Schüller et al. 2005)

The EDX spectra represent three distinguished phases as shown in the back-scattered SEM. Spectrum 1 corresponds the matrix phase, NiTi as spotted in the back-scattered images. Based on the principle of the image contrast in the back-scattered SEM, a darker colour of the phase represents a lower atomic mass of the constituent. Spectrum 2 is slightly darker than the matrix (a high-oxygen concentration was detected as indicated in arrow) for all samples together with Ni and Ti. It is also noticed

that the Ni peak in the spectrum is slightly lower than that of Spectrum 1. It is believed that these areas correspond to a Ti-rich precipitate phase, namely  $Ti_4Ni_2O_x$ . Finally, for the smallest fraction of the darkest precipitates, the carbon peak in the Spectrum 3 is greater than that for oxygen, for all samples, which is consistent with TiC formation. The presence of a small peak corresponding to Ni in the Spectrum 3 may be as a result of the neighbouring Ni of the NiTi matrix phase as the phase detected was significantly small.

#### CONCLUSION

The effect of backbone polymer in the binder system, mixed with pre-alloyed NiTi powder, on impurity contents, phase transformation temperatures and microstructures were investigated. The experimental results showed that the oxygen content of the as-sintered material increased to almost double than that for the powder state while the carbon increased by one third to half which consequently resulted in a shift of the phase transformation temperature

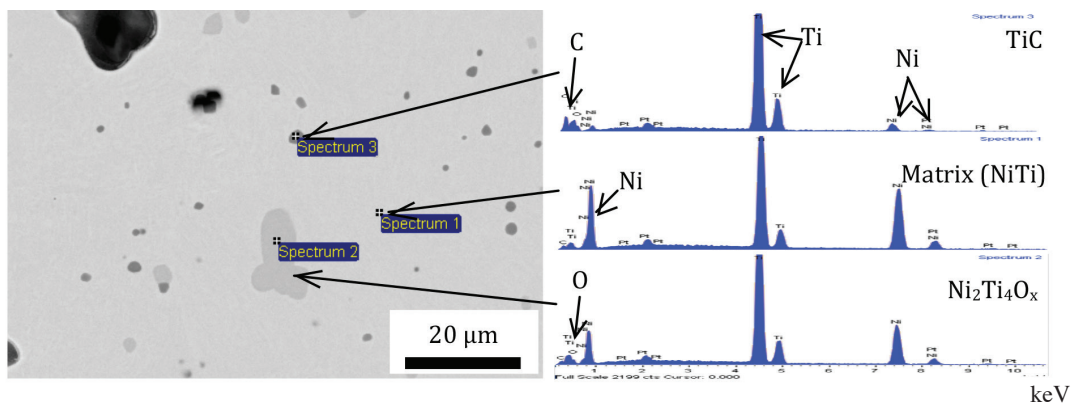


FIGURE 3. Back-scattered SEM of BS2 sample with its corresponding EDX spectra

to lower values and broadened the transformation range for the austenite to martensite transition. However, the increases in impurity content are acceptably low, when compared with the results of previous studies using wax-based binder systems, suggesting that PEG-based binder systems are an attractive proposition for MIM of NiTi alloys. The uptake of oxygen and carbon during the process led to the formation of the well known  $Ti_4Ni_2O_x$  and TiC precipitate phases which were evident from grey-scale images of back-scattered SEM.

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#### REFERENCES

- Bram, M., Ahmad-Khanlou, A., Heckmann, A., Fuchs, B., Buchkremer, H.P. & Stöver, D. 2002. Powder metallurgical fabrication processes for NiTi shape memory alloy parts. *Materials Science and Engineering A* 337(1-2): 254-263.
- Duerig, T., Pelton, A. & Stöckel, D. 1999. An overview of nitinol medical applications. *Materials Science and Engineering A* 273-275: 149-160.
- Imgrund, Ph., Rota, A., Schmidt, H. & Capretti, G. 2008.  $\mu$ -MIM: Making the most of NiTi. *Metal Powder Report* 63(5): 21-24.
- Ismail, M.H., Goodall, R., Davies, H.A. & Todd, I. 2012. Porous NiTi alloy by metal injection moulding/sintering of elemental powders: Effect of sintering temperature. *Materials Letters* 70: 142-145.
- Köhl, M., Habijan, T., Bram, M., Buchkremer, H.P., Stöver, D. & Köller, M. 2009. Powder metallurgical near-net-shape fabrication of porous NiTi shape memory alloys for use as long-term implants by the combination of the metal injection molding process with the space-holder technique. *Advanced Engineering Materials* 11(12): 959-968.
- Krone, L., Mentz, J., Bram, M., Buchkremer, H.P., Stöver, D., Wagner, M., Eggeler, G., Christ, D., Reese, S., Bogdanski, D., Köller, M., Esenwein, S.A., Muhr, G., Prymak, O. & Epple, M. 2005. The potential of powder metallurgy for the fabrication of biomaterials on the basis of nickel-titanium: A case study with a staple showing shape memory behaviour. *Advanced Engineering Materials* 7(7): 613-619.
- Mentz, J., Bram, M., Buchkremer, H.P. & Stöver, D. 2006. Improvement of mechanical properties of powder metallurgical NiTi shape memory alloys. *Advanced Engineering Materials* 8(4): 247-251.
- Mentz, J., Bram, M., Buchkremer, H.P. & Stöver, D. 2008. Influence of heat treatments on the mechanical properties of high-quality Ni-rich NiTi produced by powder metallurgical methods. *Materials Science and Engineering A* 481-482: 630-634.
- Schüller, E., Krone, L., Bram, M., Buchkremer, H.P. & Stöver, D. 2005. Metal injection molding of shape memory alloys using prealloyed NiTi powders. *Journal of Materials Science* 40(26): 4231-4238.
- Yen, F.C., Hwang, K.S., Wu, S.K. & Wu, S.H. 2011. TiNi shape memory alloys with high sintered densities and well-defined martensitic transformation behavior. *Metallurgical and Materials Transactions A* 42(8): 2431-2441.
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