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Comparison Studies on Phase Formation and Transformation Behavior between Ni-Ti and Ni-TiH_2 Synthesized via Solid State Sintering

Hafizah Hanim Mohd ZAKI[1,a *], Mohamad Hanis Mohamad SHOLIHIN1[2,b], Jamaluddin ABDULLAH[2,c], and Norshahida SARIFUDDIN[1,d]

[1]Department of Manufacturing and Materials Engineering, Kulliyyah of Engineering, International Islamic University Malaysia, Jalan Gombak, Selangor, Malaysia.

[2]School of Mechanical Engineering, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Penang, Malaysia.

[a]hafizahhanim@iium.edu.my, [b]hanissholihin@gmail.com, [c]mejamal@usm.my, [d]norshahida@iium.edu.my

ABSTRACT. Solid state synthesis is an alternative processing technique that has been attempted for producing novel-structured NiTi such as porous NiTi and other novel forms. Whilst shape memory effect is a unique advantage of NiTi shape memory alloy like, no successful attempt so far to produce single phase NiTi with good martensitic transformation behavior. As oxidation of Ti is the main problem that may retard the formation of single phase NiTi, the preliminary study of the effect of powder precursor was done. In this research, a systematic comparative investigation was performed on phase formation and transformation behavior of Ni-Ti and Ni-TiH_2 sintered specimen. It revealed that no martensitic transformation was observed for Ni-Ti specimen, attributed to minor NiTi phase formation. In addition, the XRD result of powder analysis indicates that part of Ti powder was oxidized during specimen preparation which creates imbalance composition for Ni-Ti reaction. In contrast, Ni-TiH_2 specimen displayed martensitic transformation behaviour attributed to high amount of NiTi phase formation. This reflects that the use of TiH_2 to replace Ti as powder precursor has a significant effect towards NiTi phase formation and its transformation behaviour.

Keywords: *Shape memory alloy, Transformation behavior, Solid state synthesis;*

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1. INTRODUCTION

Near-equiatomic NiTi alloys have gained much interest particularly in its porous form for its intended application in medical implant due to its good shape memory effect of monolithic NiTi. This porous form of NiTi requires solid state sintering technique, other than the conventional melt-casting method. Several research groups have published studies on solid state synthesis of NiTi from elemental powder of Ni and Ti by using different techniques such as conventional pressureless powder sintering [1], hot isostatic pressing [2], self-propagating high temperature synthesis [3], spark plasma sintering [4,5], and microwave sintering [6], though little success has been achieved in terms of satisfactory shape memory behaviour, as evidenced by the absence of visible applications of these materials.

The desired phase for shape memory effect is the equiatomic NiTi. Almost all NiTi produced via solid state sintering from elemental powder of Ni and Ti, have complex microstructures involving multiple phases including Ti_2Ni and $TiNi_3$ [1]. These phases do not exhibit martensitic transformation and destroy the shape

memory behaviour of the alloys. It is believed that the main obstacle to producing single phase NiTi is the oxidation. During sintering, Ti is easily oxidized to form TiO_2. The formation of this oxide may depletes Ti content for Ni-Ti reaction, leaving abundance of Ni that may reacts with remaining Ti to form $TiNi_3$. As a result, multiple phases may form.

Therefore, this research investigates the preliminary effect of Ti and TiH_2 powder precursor mixed with Ni on phase formation and transformation behaviour of NiTi. The use of TiH_2 to replace Ti as powder precursor may protect the specimen from oxidation as high decomposition temperature of TiH_2 at above 400 °C may prevent the formation of TiO_2 not only during specimen preparation but also during sintering.

2. MATERIALS AND METHODS

In this work, high purity Ni (particle size < 30 μm) and TiH_2 (particle size ≤ 44 μm) have been mixed at equiatomic composition by means of low energy ball milling for 24 hours. After mixing, the powder mixture was cold compacted into cylindrical shape of ϕ12 x 4 mm to 3 tonnes of force. Then, the specimens were sintered at different temperatures and time in flowing argon. Phase formation analysis was carried out using scanning electron microscope (SEM) of Hitachi S-3400N equipped with energy dispersive spectroscopy (EDS) and X-ray diffractometer (XRD). Quantitative analysis of the area fractions of phases formed was performed by means of image analysis of SEM backscattered micrographs using ImageJ software, free software provided by the National Institute of Health (NIH), USA. This phase fraction analysis was done by differentiating contrast levels among the different phases present which had been previously identified through EDS. Differential scanning calorimetry (DSC) was conducted using a TA Q20 instrument to analyse martensitic phase transformation behaviour of the sintered specimens. The occurrence and the magnitude of this martensitic transformation are good indicators of the formation of the B2-NiTi phase in the specimens, an essential requirement for shape memory effect.

3. RESULTS AND DISCUSSION

3.1 Phase Characterization. Fig. 1 shows the SEM micrographs with EDS analysis of Ni-Ti specimen sintered at different temperatures for 6 hours. For the specimen sintered at 750 °C, the Ni(Ti) solid solution containing >5 at%Ti phase appears as isolated islands whereas Ti with <1 at %Ni presents in a matrix structure. The formation of Ti_2Ni indicates that the diffusion process has already commenced at 750 °C. The specimen sintered at 850 °C and 900 °C showed an increased degree of diffusion. The dominant structure is the products formed in between the original Ni(Ti) and Ti(Ni), which have obviously been reduced in volume. The enlarged view reveals that the products contained several phases, including $TiNi_3$, NiTi and Ti_2Ni. Referring to high magnification of Fig. 1I, it is observed that NiTi formed in an extensive cob-web structure inside the Ti_2Ni phase, appearing to propagate from the Ni side towards the Ti side. In most parts, the NiTi network has consolidated into continuous matrix, with small Ti_2Ni entrapped inside NiTi. In the specimen sintered at 1080°C, only three phases were found, i.e., NiTi, Ti_2Ni and $TiNi_3$, where NiTi forms the continuous matrix with $TiNi_3$ network emerged within the NiTi matrix.

Fig. 2 shows the SEM images of the microstructures of the Ni-TiH_2 specimen sintered at different temperatures from 750 °C to 1080 °C for 6 hours. Specimen sintered at 750 °C shows the formation of multiple phases such as NiTi, Ti_2Ni, $TiNi_3$, and Ni(Ti). When sintering temperature increases to 850 °C, NiTi increased aggressively, forming the matrix with small patches of Ti_2Ni scattered everywhere. The NiTi matrix is heavily embedded with "needles-like structure" as indicated in high magnification figure as indicated in Fig. 2(b). This needles-like structure is believed to be Ni-rich precipitates, Ni_4Ti_3 as reported by [7]. Increasing sintering temperature to 930 °C and 1080 °C, the amount of Ti_2Ni phase reduced, while more Ni_4Ti_3 precipitates were observed in the NiTi matrix.

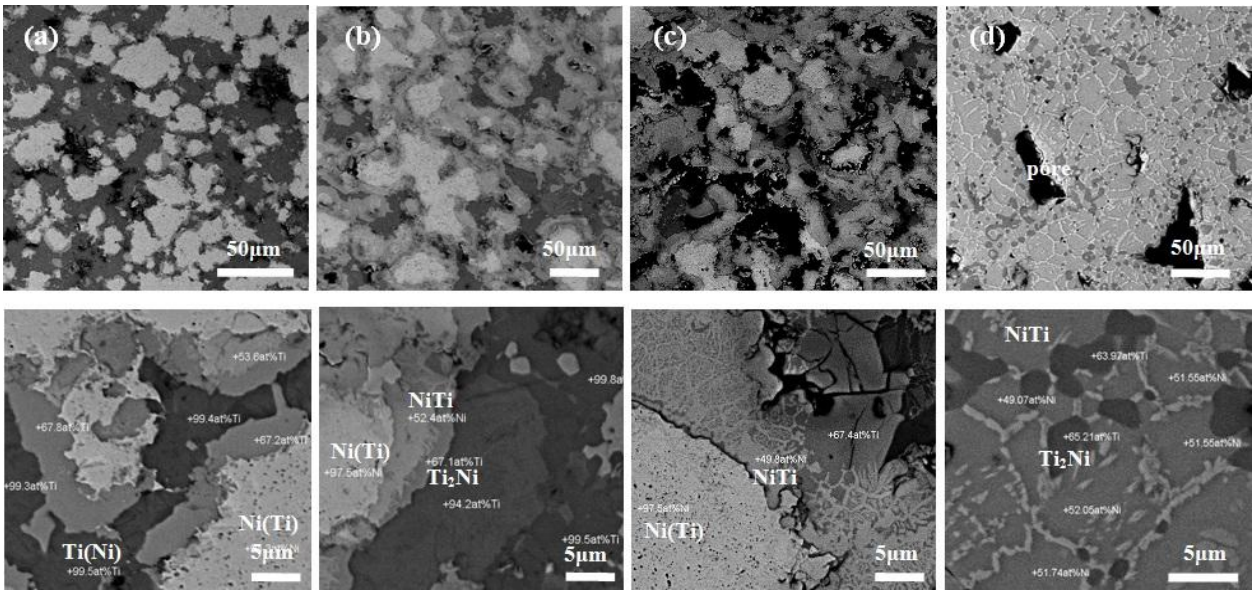

Fig. 1 SEM micrographs of Ni-Ti sintered at different temperatures (a) 750 °C, (b) 850 °C, (c) 900 °C and (d) 1080 °C for 6 hours. The micrographs shown on top are of lower magnifications and the micrographs shown on bottom are of high magnifications

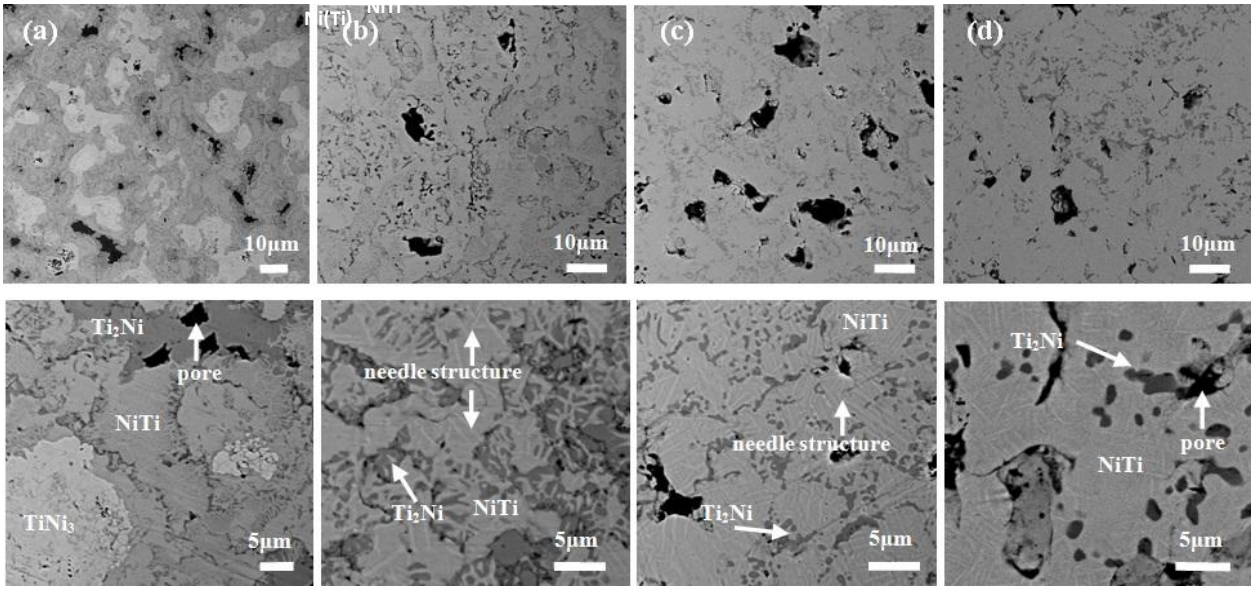

Fig. 2 SEM micrographs of Ni-TiH_2 sintered at different temperatures (a) 750 °C, (b) 850 °C, (c) 930 °C and (d) 1080 °C for 6 hours. The micrographs shown on top are of lower magnifications and the micrographs shown on bottom are of high magnifications

Fig. 3 shows the XRD spectra for Ni-Ti and Ni-TiH_2 specimen sintered at different temperature for 6 hours. For Ni-Ti specimen, at 750 °C, almost no new phase formation took placed except Ti_2Ni phase. However, the EDS analysis confirmed that NiTi, Ti_2Ni, and $TiNi_3$ were all present as shown in Fig. 1(a). This is due to the limitation of XRD in detecting phases of low volume fractions less than 5%. NiTi in the form of austenite was observed to form in the specimen sintered at 850 °C, however the original precursor of Ni is still the dominant phase even after 900 °C, implying early stages of diffusion sintering. Increasing the sintering temperature to 1080 °C led to the disappearance of both Ni and Ti where only three phases were observed, i.e., NiTi, Ti_2Ni and $TiNi_3$ with NiTi being the dominant phase and consistent with the SEM observation (refer

Fig. 1(d)). In contrast, for Ni-TiH_2 specimen, the peaks of B2-NiTi increased as the temperature increased. At higher temperature, the diffusion rate is greater, thus leading to more phase formation at the expense of Ni and Ti.

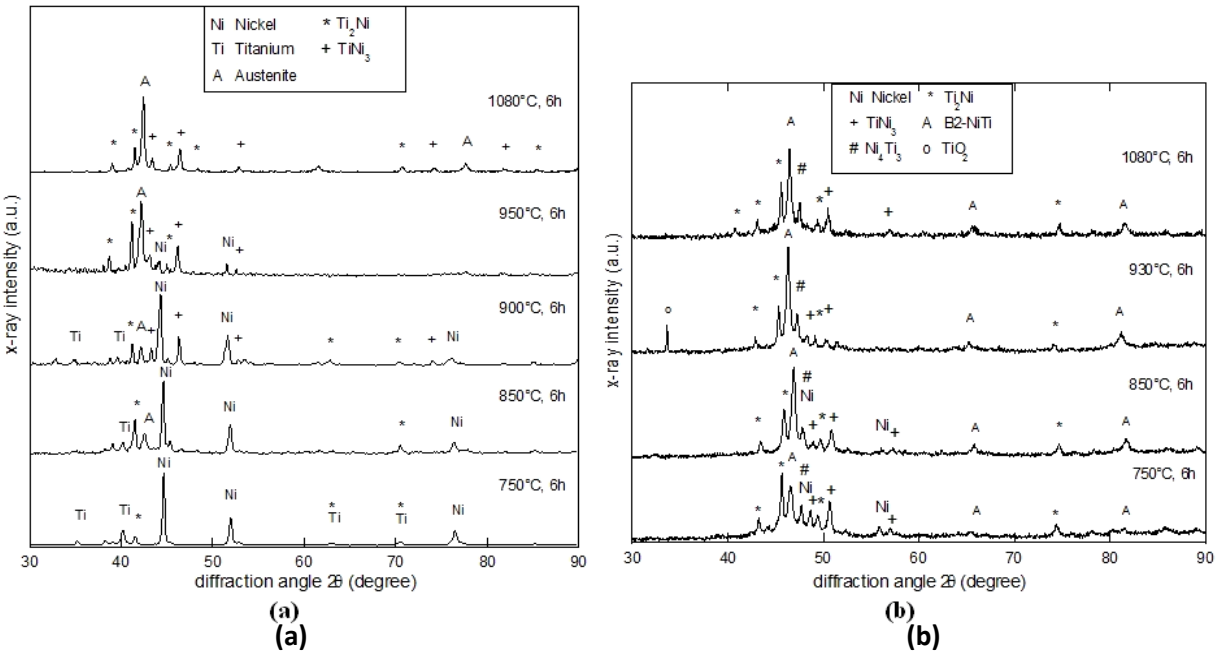

Fig. 3 XRD spectra of (a) Ni-Ti (b) Ni-TiH_2 specimen sintered at different temperatures for 6 hours

3.2 Phase Fraction Analysis. Fig. 4 shows NiTi area fractions of both Ni-Ti and Ni-TiH_2 specimen sintered at different temperature to see the effect of replacing the powder precursor of Ti to TiH_2 on NiTi phase fraction. Surprisingly, the area fraction of NiTi increased aggressively to double (in average) for each temperature. This reflects that the use of TiH_2 as powder precursor to replace Ti can effectively increase the total area fraction of NiTi by reducing the oxygen contamination that cause oxidation during specimen preparation and sintering.

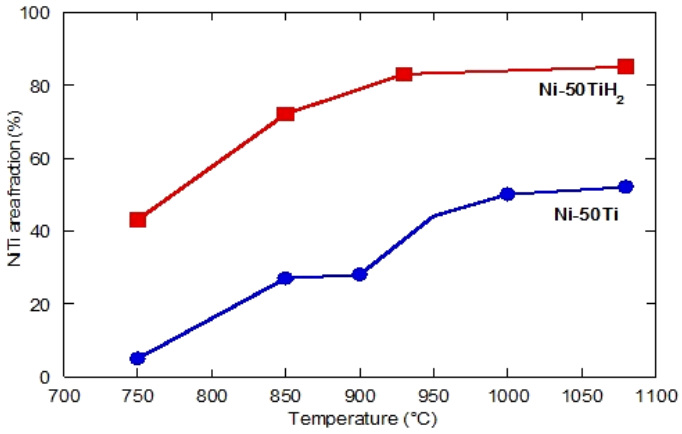

Fig. 4 Comparison of NiTi phase fraction between specimen Ni-TiH_2 and Ni-Ti sintered at various temperatures for 6 hours duration as determined by ImageJ software

3.3 Oxide Analysis. Ni+Ti powder mixture was further analysed using XRD to detect the oxide formation at this stage. The result of Ni+Ti powder mixture was then compared to the as-received Ti powder. According to XRD result as shown in Fig. 5, only Ti peaks were observed for as-received Ti powder, implying no oxidation was detected at this stage. However, the TiO_2 peaks were detected for Ni+Ti powder mixture. This indicates that part of Ti powder was oxidized during specimen preparation i.e. ball milling. As a conclusion, the loss of Ti due to oxidation during specimen preparation (mixing) creates imbalance composition for Ni-Ti reaction, thus formation of single phase NiTi can't be achieved using Ti as powder precursor. This implies that oxidation impedes the formation of single phase NiTi.

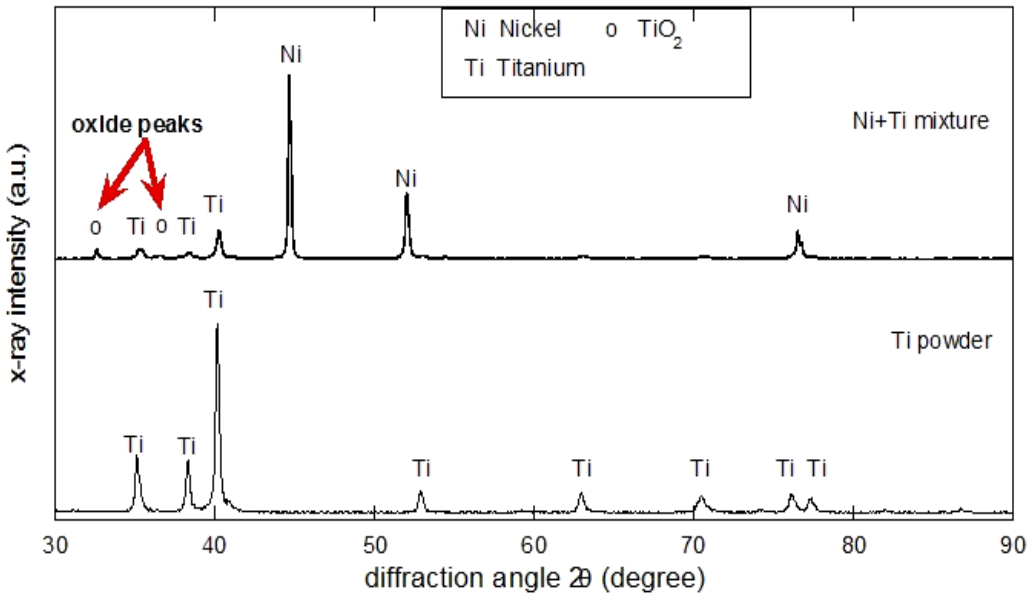

Fig. 5 XRD spectra of Ti powder and powder mixture of Ni+Ti after ball milling

3.4 Transformation behaviour. Fig. 6 shows the plot of DSC curves of Ni-Ti and Ni-TiH_2 specimen sintered at different temperatures. For Ni-Ti specimen, none of the specimens show transformation either on cooling or heating, even though they have significant amount of B2-NiTi phase present in the matrix. One possible explanation for the absence of transformation in these specimens is the high Ni content in the B2-NiTi phase as measured by EDS. According to SEM Fig. 1, it is evident that B2-NiTi phase generally contained >52 at%Ni. It is known that B2→B19' martensitic transformation temperatures are highly dependent on the Ni content in NiTi. The transformation temperatures decrease rapidly with increasing Ni content in the B2-NiTi and no transformation can be observed for the specimen with Ni content >51.7 at% [8]. However, transformation peaks were detected for Ni-TiH_2 specimens. For specimen sintered at 750 °C, transformation occurs both on cooling and heating with $\Delta H_{A\rightarrow M}$ = 3.04 J/g and $\Delta H_{M\rightarrow A}$ = 1.6 J/g, respectively. The enthalpy change increased with increasing sintering temperature both upon cooling and heating, implying more B2-NiTi participate in the transformation. However, the overall total value of enthalpy change (≤9 J/g) is still lower compared to the bulk NiTi alloy (~24-28 J/g) [9].

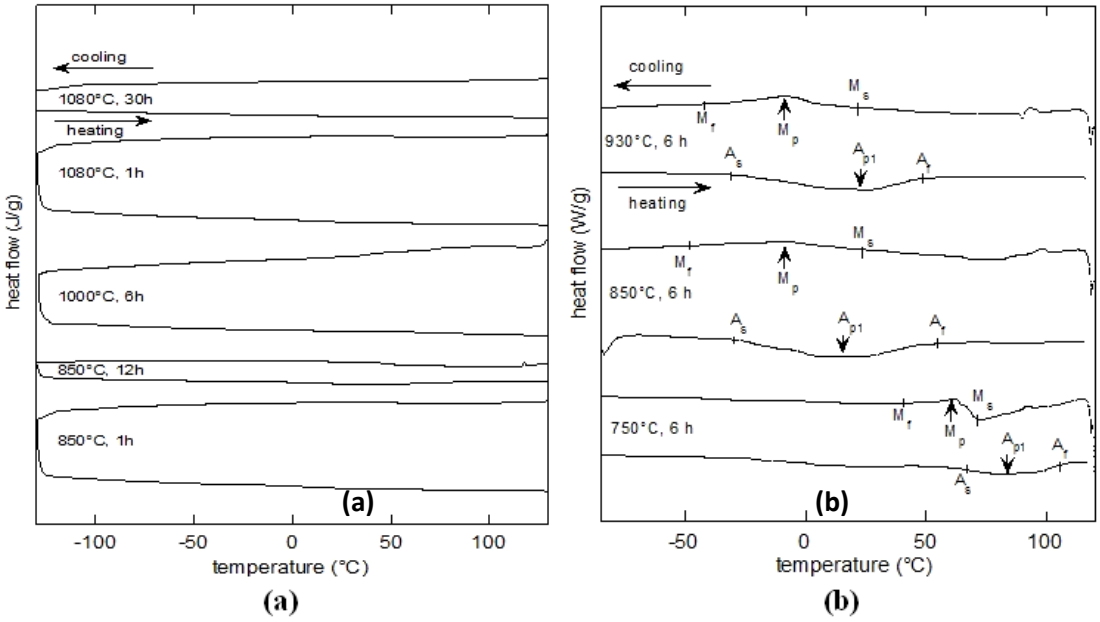

Fig. 6 DSC curves of (a) Ni-Ti (b) Ni-TiH_2 specimens sintered at different temperatures and times

Table 1 Transformation temperature and enthalpy change for Ni-TiH_2 specimen sintered at different temperatures for 6 hours

Specimen	A→M				M→A				
	M_s (°C)	M_f (°C)	M_p (°C)	ΔH (J/g)	A_s (°C)	A_f (°C)	A_{p1} (°C)	A_{p2} (°C)	ΔH (J/g)
750 °C	67.2	47.5	62.8	3.04	62.7	105	83.9	-	1.6
850 °C	15.5	-50	-7.58	4.0	-35	53	12.5	-	8.03
930 °C	30	-43	-8.21	5.08	-36	52	23.77	-	9.06

4. SUMMARY

For Ni-Ti specimen, no martensitic transformation was observed attributed to minor NiTi phase formation. In contrast, Ni-TiH_2 specimen has high amount of B2-NiTi and displayed martensitic transformation behavior. This reflects that the use of TiH_2 to replace Ti as powder precursor has a significant effect towards NiTi phase formation and its transformation behaviour.

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