

A Study of CaH₂ Effectiveness as Oxidation Prevention in Solid State Sintering of Single Phase NiTi Alloy

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Abstract: This research aims to study the conditions that may produce single phase NiTi for desirable shape memory effect under solid state by suppressing the oxide levels using CaH₂ as in-situ reducing agent. A systematic comparative investigation was made on phase formation and their transformation behavior. Phase formation analysis was carried out using Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS) and X-Ray Diffractometer (XRD). The transformation behaviour was studied by means of Differential Scanning Calorimetry (DSC) measurements. Thermomechanical analysis was conducted using Thermomechanical Analyzer (TMA). The study revealed that single phase NiTi was successfully formed from Ni-TiH₂ specimen sintered at 930°C for 3 h under CaH₂ reducing environment with good enthalpy change of $\Delta H_{A-M} = 26 \text{ J g}^{-1}$ and $\Delta H_{M-A} = 25.5 \text{ J g}^{-1}$ upon cooling and heating, respectively. However, the recovery strain reaches 0.75% at maximum 8 N applied load which is still below than the reported bulk NiTi.

Key words: Solid state diffusion, shape memory alloys, martensitic transformation, enthalpy change, Malaysia

INTRODUCTION

Solid state synthesis of NiTi alloy has gained much interest particularly in its porous form for its intended application in medical implant due to its good pseudoelasticity and shape memory effect of monolithic NiTi (Otsuka and Wayman, 1998). Apart from that, monolithic NiTi offers better mechanical properties such as relatively low stiffness to prevent stress shielding, high strength to prevent deformation or fracture and high toughness to avoid brittle failure. Thus, the combination of these properties makes porous NiTi as promising materials than any other biocompatible materials. Porous TiNi carries desirable property much needed in medical implant where pores can encourage tissue in-growth which is not possible with conventional dense metal implants (Jorma, 1999; Kujala, 2003).

The studies on porous NiTi are mostly on synthesis by various means such as combustion synthesis (Chu *et al.*, 2004, 2006; Li *et al.*, 2000), pressureless powder sintering (Laeng *et al.*, 2007; Hey and Jardine, 1994), hot isostatic press (McNeese *et al.*, 2000; Greiner *et al.*, 2005) and spark plasma sintering (Shearwood *et al.*, 2005; Ye *et al.*, 1998) to achieve good

mechanical properties and pores morphology that resembles bones and its long-term biocompatibility with human body. Although, there were numerous attempts reported in the literature to produce single phase TiNi, no conclusive work has been done to explain the mechanisms of TiNi phase formation in solid state. The phase formation in porous TiNi under solid state shows largely multi-phase structure consisting of Ti (Ni), Ti₂Ni, TiNi, TiNi₃ and Ni (Ti) (Laeng *et al.*, 2007) where Ti₂Ni and TiNi₃ can not be completely removed even by subsequent post treatment since they are thermodynamically stable (Greninger and Mooradian, 1938). The formation of undesired phases may jeopardize the shape memory properties of the alloys synthesized.

It is believed that the main obstacle to producing single phase NiTi is the oxidation problem. Ti is oxidized easily to form TiO₂ at the surface owing to its higher affinity to oxygen. Another difficulty is the formation of Ti₄Ni₂O_x (0 < x ≤ 1) which appears and is always misinterpreted as Ti₂Ni because of the structure similarity between the two phases (Nishida *et al.*, 1986). The formation of these two oxides may reduce the Ti content for the Ni-Ti reaction; thus, creating intermetallic phases such as TiNi₃ due to unbalanced composition existing between Ni and Ti.

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Single phase NiTi is an indicator for having good shape memory effect. This research aims to study the conditions that may produce single phase NiTi by using different starting powder together with the oxidation prevention measures. In this case, CaH₂ powder was used as reducing agent.

MATERIALS AND METHODS

In this research, high purity Ni (30 μm), Ti (50 μm) and TiH₂ (44 μm) were used to form near equiatomic mixture. These powders were mixed at equiatomic composition (Ni:Ti and Ni:TiH₂) by means of low energy ball milling for several hours to obtain homogenous mixing. After mixing, the powder mixtures were cold compacted into cylindrical shape of φ12×4 mm under 3 tons of force. The specimens were sintered at 930°C for 3 h to study the effect of different starting powder with and without reducing agent of CaH₂.

Microstructural analyses were examined using a SEM equipped with an EDS for compositional analysis. An XRD was conducted for phase identification. Phase transformation behavior was studied by DSC measurement using TA Q10 DSC machine at a heating/cooling rate of 10°C min⁻¹. Thermomechanical testing was carried out using the TMA 7 Perkin Elmer with a heating/cooling rate of 5°C min⁻¹ with different constant load; 2, 4 and 8 N.

RESULTS AND DISCUSSION

Phase characterization: Figure 1 shows a collection of SEM micrograph of the sintered Ni-Ti and Ni-TiH₂ of equi-atomic ratio prepared from elemental Ni and Ti or TiH₂ powders. All the samples were sintered at 930°C for 3 h. This temperature is well below the eutectic point at 942°C to avoid melting and to assure all solid state reaction during sintering. Both Ni-Ti specimens are found to have practically the same microstructure with multiple phases such as Ti₂Ni, TiNi₃ and TiNi were observed as indicated in Fig. 1a-d, respectively. For Ni-TiH₂ specimen sintered without CaH₂, the structure shows a continuous NiTi matrix embedded with “needles-like structure” of Ti₃Ni₄ as indicated in Fig. 1e and f. Based on EDS analysis, the average composition of the NiTi-Ti₃Ni₄ matrix is 55% at Ni, 2% lower than the actual Ni content in Ti₃Ni₄ (57% at Ni). This is due to the mixture of two phases (NiTi-composition 51% at Ni and Ti₃Ni₄-composition 57% at Ni). The used of TiH₂ compound to replace Ti led to an increase of NiTi volume fraction to 85%. In contrast, when Ni-TiH₂ was sintered under CaH₂ reducing environment only NiTi phase was formed as indicated in Fig. 1g and h.

Figure 2 shows a comparison set of XRD spectra for Ni-Ti and Ni-TiH₂ specimens after sintering. The bottom 3 specimens show the presence of multiple phases of Ti₂Ni, TiNi and TiNi₃ with TiNi as a major phase. Some residual Ni is still visible in the XRD spectrum for both Ni-Ti specimens whereas significant reduction of Ni peak was observed for Ni-TiH₂ specimen without CaH₂. No peak of Ti was detected, although a small fraction of Ti (Ni) was found in the SEM image (Fig. 1c and d). This is due to lower intensities of Ti peaks compared to those of the Ni peaks. In contrast, only B2-NiTi peaks were detected for Ni-TiH₂ specimen sintered with CaH₂. This is consistent with SEM observation where only single phase NiTi present in the specimen as evident in Fig. 1d.

The used of TiH₂ as starting powder and also the CaH₂ as reducing agent has great influenced on formation of single phase NiTi. The TiH₂ can reduce the contamination during sample preparation and also protect the specimen from oxidation at early stage of sintering. TiH₂ decomposed at ~400°C, therefore supplies fresh Ti in atomic form which is highly reactive for alloying with Ni to further enhance for Ni-Ti reaction kinetics. In addition, the decomposition of CaH₂ at above ~816°C can protect the specimen during sintering at high temperature. The Ca act as oxygen getter, therefore, reduce the oxygen level in the environment. A significant reduction of this oxidation creates the balance composition between Ni and Ti for Ni-Ti reaction and this led to formation of single phase NiTi.

DSC analysis: Figure 3 shows the DSC curves for Ni-Ti and Ni-TiH₂ specimens sintered at 930°C for 3 h. All the values including A_s, A_f, A_{p1}, A_{p2}, M_s, M_f and M_p are measured in Table 1. No transformation peak was detected for both Ni-Ti specimen. This attributed to the low volume fraction of the B2-NiTi phase and also the high Ni content in the NiTi matrix. It is known that B2-19' martensitic transformation temperatures are dependent highly on the Ni content in NiTi. The transformation temperatures decrease rapidly with increasing Ni content in the B2-phase (Otsuka and Wayman, 1998). For Ni-TiH₂ specimen sintered without CaH₂, small transformation peak was detected both on cooling and heating with enthalpy change of ΔH_{A-M} = 7.9 J g⁻¹ and ΔH_{M-A} = 13.2 J g⁻¹. This is consistent with the SEM observation where NiTi is a majority phase (constitute of 85%). In this case not all B2-NiTi observed is active in participating in the transformation. This may be attributed to the high Ni content in some parts of the NiTi phase. The Ni-content in TiNi may be too high that it does not transform. Meanwhile, Ni-TiH₂ specimen sintered under CaH₂ reducing environment displays better A→M (cooling) and M→A (heating) transformation

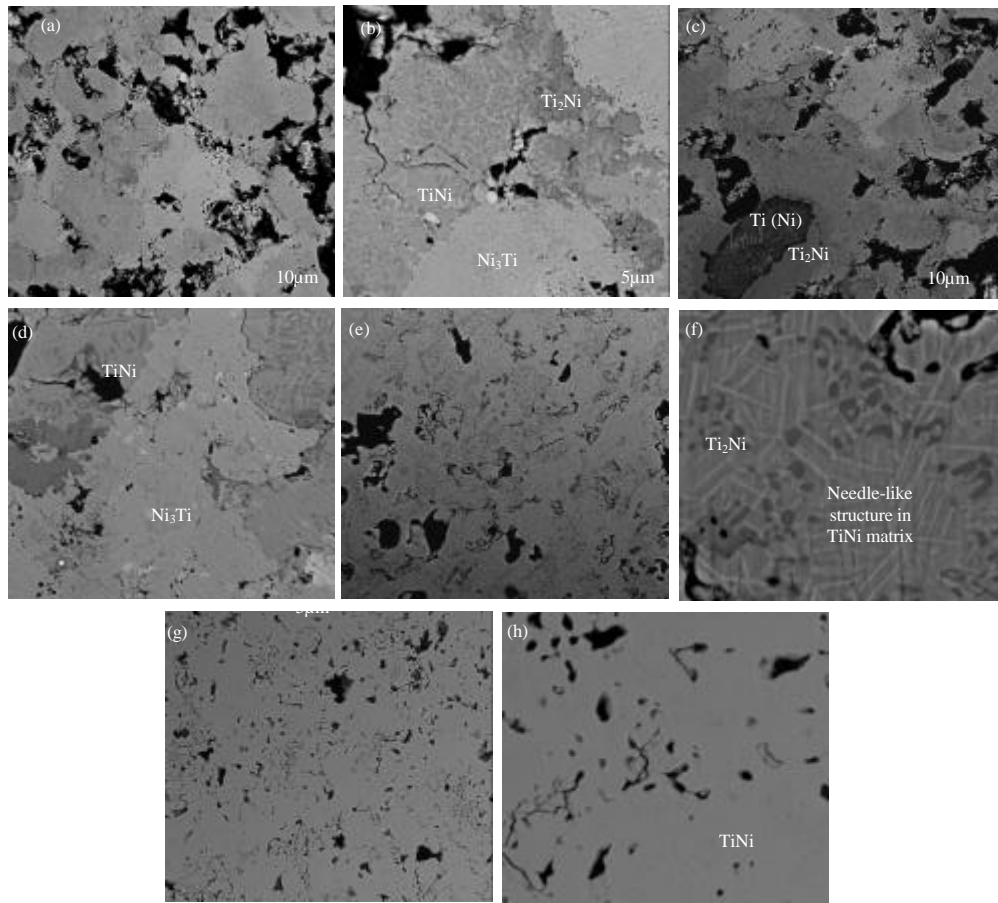


Fig. 1: SEM with backscattered image of specimens sintered at 930°C for 3 h: a, b) Ni-Ti (no CaH₂); c, d) Ni-Ti (CaH₂); e, f) Ni-TiH₂ (no CaH₂); g, h) Ni-TiH₂ (CaH₂). The images shown on the left are of lower magnifications and the images shown on the right are of high magnifications

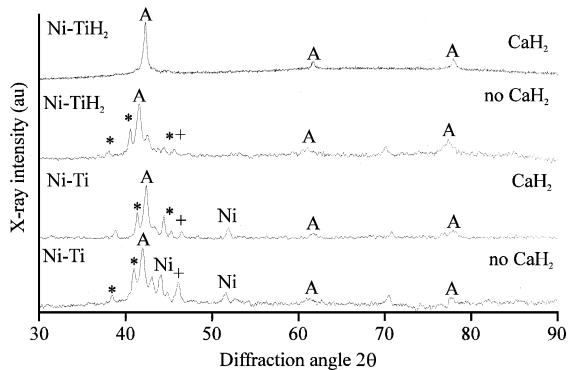


Fig. 2: XRD spectra of specimens of different starting powder of Ni-Ti or Ni-TiH₂ with equi-atomic composition sintered at 930°C for 3 h. Two specimens were sintered under reducing environment of CaH₂; Ni = Nickel; * = Ti₂Ni; + = TiNi₃; A = B2-NiTi

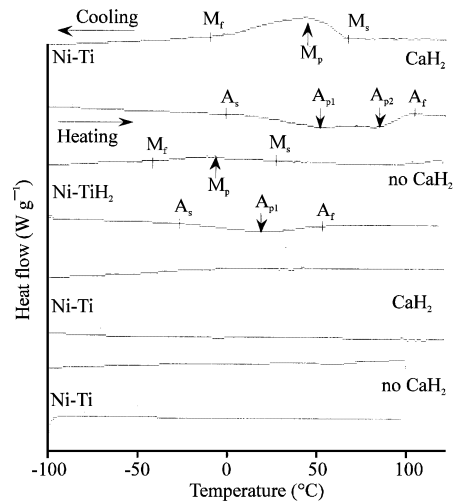


Fig. 3: DSC curves of Ni-Ti and Ni-TiH₂ specimens sintered at 930°C for 3 h with and without CaH₂

Table 1: DSC measurement of enthalpy changes (ΔH), peak transformation (M_p and A_p) and transformation temperatures for Austenite (A)-Martensite (M)

Specimen	Temperature Sintering		A-M			ΔH (J g ⁻¹)	M-A				ΔH (J g ⁻¹)
	(°C)	condition	M_s (°C)	M_f (°C)	M_p (°C)		A_s (°C)	A_f (°C)	A_{p1} (°C)	A_{p2} (°C)	
Ni-TiH ₂	930	No CaH ₂	34.0	-54.5	10.0	7.9	-37.5	60.5	18.9	-	13.2
Ni-TiH ₂	930	CaH ₂	63.3	-14.5	41.9	26.0	5.7	101.2	53.1	85	25.5

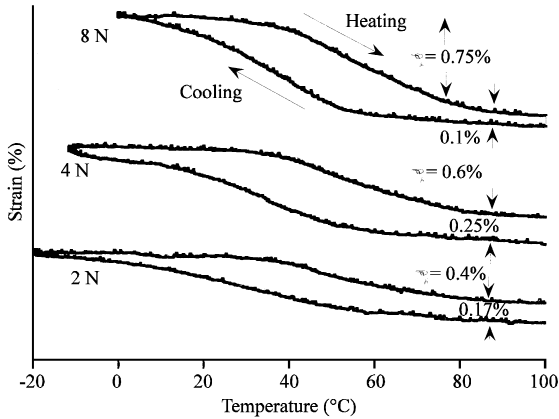


Fig. 4: TMA curves of Ni-TiH₂ specimens subjected to different applied loads

with enthalpy change of $\Delta H_{A-M} = 26 \text{ J g}^{-1}$ and $\Delta H_{M-A} = 25.5 \text{ J g}^{-1}$, respectively. These enthalpy values agree with the values usually found in melt cast Ti-rich alloy.

TMA analysis: Figure 4 shows the strain vs. temperature curves for Ni-TiH₂ specimens sintered under CaH₂ reducing environment. This specimen was subjected to three different constant load, i.e., 2, 4 and 8 N. When the applied load increases, the recovery strain (E_A) increases and reaches maximum of 0.75% for 8 N. However, the shape memory is not fully completed upon heating where small residual strain being observed at all applied loads. These values are still lower than the reported NiTi bulk (Duerig *et al.*, 1990).

CONCLUSION

Single phase NiTi was successfully produced under several conditions:

- The used of Ni and TiH₂ as starting powder reduced the oxygen contamination at early stage of sintering
- The used of CaH₂ as reducing agent where upon decomposition, the Ca act as oxygen getter and prevent from further oxidation of Ti and TiNi at high temperature

This specimen shows good transformation behavior similar to dense NiTi, however, the recovery strain is still below than the reported bulk NiTi.

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