Effect of different reducing agents on phase formation and transformation behaviour of Ni-Ti shape memory alloy

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Abstract. In this study, NiTi synthesized via solid-state sintering from Ni-TiH₂ powders in reducing environments using (i) CaH₂, (ii) MgH₂ and (iii) CaH₂ and MgH₂ as in situ reducing agent were investigated. The phase formation was characterized by means of scanning electron microscope (SEM), energy-dispersive spectroscope (EDS) and powder X-ray diffraction (XRD), while transformation behavior was analyzed using differential scanning calorimetry (DSC) measurement. Among these three reducing agents, synthesis in reducing environment using CaH₂ as in situ reducing agent resulted in the formation of single phase NiTi with enthalpy change of 25–26 J/g, which is similar to melt-cast NiTi alloys. Specimens sintered in reducing environments using MgH₂ and MgH₂+CaH₂ as in situ reducing agents have lower enthalpy change, ~16–21 J/g compared to CaH₂. This work established the fact that, synthesis in different reducing environment appears to have profound effects on the phase formation and transformation behavior of NiTi.

1. Introduction

Near-equitatomic NiTi alloy has ranges of useful engineering properties besides their unique shape memory properties. While most current applications of NiTi are made of conventional alloys in solid forms such as wires, plates, and thin walled tubes [1], keen interests have been given to novel physical forms of NiTi. Such novel forms often require novel fabrication and processing techniques other than the conventional method of melting, casting, and metalworking. For example, thin films are produced by sputter deposition [2, 3], multilayer NiTi are produced by diffusion annealing of ultrafine laminates of Ni and Ti [4], ribbons are produced by melt-spinning method [5], porous NiTi [6, 7], and gradient composition NiTi [8] are obtained by solid state sintering of elemental powders. Active exploration of possible means to achieve porous single phase NiTi has included various solid state sintering such as conventional furnace sintering [9], hot-isostatic pressing (HIP) [10], self-propagating high temperature synthesis (SHS) [11], spark plasma sintering [12], and microwave sintering [13], though little success has been achieved in terms of satisfactory shape memory behavior as evidenced by the absence of visible applications of these materials.

The formidable challenge of obtaining NiTi via solid state with good shape memory behaviour, which can resemble the properties of melt-cast NiTi is yet to be achieved. Various sintering parameters and sintering techniques have been employed which did not lead to formation of single
phase NiTi. Therefore, the question arises whether single phase NiTi can be formed via solid state synthesis from elemental powder. In addition, the study on oxidation by Shearwood, Fu [14] contributed towards an idea that the oxidation may retard the formation of single phase NiTi, but no further or repeatable works in the same nature have been done. Therefore, this research is conducted to investigate whether the formation of single phase NiTi via solid state synthesis from elemental powder is feasible. In this case, the sintering was conducted in protected environment i.e. reducing environment to protect the specimen from oxidation. The effect of using different reducing agents such as CaH$_2$, MgH$_2$ and a mixture of CaH$_2$ and MgH$_2$ on NiTi phase formation is discussed. The transformation behaviour of Ni-Ti synthesized in these reducing environments is also investigated.

2. Experimental procedures

2.1 Specimen Preparation

In this work, high purity Ni (average particle size < 30 µm) and TiH$_2$ (mean particle size = 44 µm) were used to form near equiatomic mixture. These powders were mixed at equiatomic composition by means of low energy ball milling for 24 hours to obtain homogenous mixing. 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 930 °C for 3 hours in reducing environment. This reducing environment was achieved using CaH$_2$ and MgH$_2$ powder as in-situ reducing agent to prevent oxidation. Approximately 200 to 300 mg of CaH$_2$ or/and MgH$_2$ powder were poured on the exposed surface of the specimen.

For solid state diffusion synthesis, the sintering must be conducted at below 1310 °C temperature to prevent melting. There is also an eutectic point on the Ti side at 942 °C. Based on these considerations, the specimens were sintered below the eutectic point at 942 °C, to avoid partial melting and to ensure solid state reaction during sintering.

2.2 Specimen Characterization and Analysis

For sampling, a thin slice was cut off from the middle of the cylindrical sample for X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) characterization. Microstructural analyses were examined using backscattered electron imaging (Hitachi S-3400N) equipped with energy dispersive spectroscopy (EDS). After XRD analysis, a small piece was cut off from the middle of the XRD sample with approximately 1x2 mm for differential scanning calorimetric (DSC). Phase transformation behavior was studied by DSC measurement using TA Q10 DSC machine at a heating/cooling rate of 10 °C/min.

3. Results and Discussion

Figure 1 shows a collection of SEM micrographs of the Ni-TiH$_2$ specimens sintered at 930 °C for 3 hours in three different reducing environments. For the specimen sintered using MgH$_2$ as a reducing agent, there are many tiny spots, which correspond to Ti-rich phase with composition of Ti-57.3 at% and Ni-42.7 at% in NiTi matrix. According to XRD result as indicated in figure 2, small peaks of Ti$_2$Ni were observed along with high intensity B2-NiTi peaks. Therefore, this Ti-rich phase is referred to as Ti$_2$Ni phase. For the specimen sintered using CaH$_2$ as reducing agent, only single phase NiTi was observed with no Ti$_2$Ni phase. This observation is consistent with the XRD result where only peaks of B2-NiTi were formed. Meanwhile, specimen sintered in reducing environment of MgH$_2$ mixed with CaH$_2$ shows small patches of Ti$_2$Ni with composition of Ti-64.9 at%, Ni-35.1 at%. The formation of Ti$_2$Ni phase in NiTi matrix is similar to specimen sintered in MgH$_2$ reducing environment, except the composition of Ti is higher.
Figure 1. SEM micrograph showing single phase NiTi formed using different reducing agent of (a) MgH$_2$ (b) CaH$_2$ and (c) mixture of MgH$_2$ and CaH$_2$. The micrographs shown on the top are of lower magnifications and the micrographs shown on the bottom are of high magnifications.

Figure 2. XRD spectrum of sintered specimen at 930 °C for 3 hours using different reducing agents.

Figure 3 shows DSC curves for the specimen sintered at 930 °C for 3 hours in three different reducing environments. Referring to DSC curves, all specimens exhibited single peak A↔M martensitic transformation both upon cooling and heating, except for the specimen sintered in a CaH$_2$ reducing environment where the double-peaks referred to as A$_{p1}$ and A$_{p2}$ were observed upon heating.
These peaks are not associated with R-phase, instead this phenomenon is due to inhomogenous distribution of Ni composition exist within the individual grains as the transformation temperatures are very sensitive to composition.

For the specimen sintered using MgH₂ as a reducing agent, transformation peaks were detected both on cooling and heating with enthalpy change of ΔH_{A→M} = 18.7 J/g and ΔH_{M→A} = 21.6 J/g, respectively. For the specimens sintered in CaH₂ and MgH₂ reducing environment, intermediate value of enthalpy change was measured with 16.2 J/g and 19.6 J/g both upon cooling and heating, respectively. However, this value is still lower than the value measured for the specimens sintered in the CaH₂ reducing environment. This attributed to the formation of Ti₂Ni phase in NiTi matrix (refer figure 1) which lowered the enthalpy value as this phase does not involved in the martensitic transformation. However, this specimen still exhibited good transformation behaviour if compared to synthesis in non-reducing environment as reported by [9].

![DSC curves of Ni-TiH₂ specimens sintered at 930 °C for 3 hours using different reducing agents](image)

Figure 3. DSC curves of Ni-TiH₂ specimens sintered at 930 °C for 3 hours using different reducing agents

Figure 4 shows the EDS plot of Ni composition in the NiTi matrix. The overall Ni content in the NiTi matrix for the specimen sintered in a CaH₂ is below the martensitic transformation (MT) limit, therefore all the B2-NiTi phase is participating in the transformation, thus gives high value of enthalpy change. For the specimen sintered in the MgH₂ reducing environment, the Ni content is still below the MT limit. In addition, the Ni content is almost consistent and did not fluctuate too much as observed for the specimen sintered in the CaH₂ reducing environment, implying homogenous distribution of Ni content in NiTi matrix, therefore resulting in single peak transformation both on cooling and heating. As discussed previously, the only reason it has a lower enthalpy change value than CaH₂ is due to the formation of Ti₂Ni phase.

Meanwhile, for the specimen sintered in both MgH₂ and CaH₂ reducing environment, part of Ni content is exceeding MT limit, therefore this particular B2-NiTi did not participated in the
transformation. This explains the lower value of enthalpy change obtained by this specimen compared to the specimen sintered in an MgH$_2$ reducing environment.

![Figure 4](image)

**Figure 4.** The EDS plot of Ni content in NiTi matrix of Ni-50TiH$_2$ specimen sintered at 930 °C for 3 hours in different reducing environments

4. **Conclusion**

In summary, synthesis of Ni-TiH$_2$ in reducing environment especially CaH$_2$ as an in situ reducing agent resulted in the formation of single phase NiTi with good enthalpy change (~25-26 J/g) similar to the melt-cast NiTi alloys (~24-28 J/g). Although specimens synthesized in MgH$_2$ and MgH$_2$+CaH$_2$ did not produced single phase NiTi, both specimen exhibited good transformation peak both on cooling and heating. This shows that synthesis in different reducing environment appears to have profound effects on formation of single phase NiTi and transformation behavior of NiTi synthesized in solid state.

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