Comparison studies on solid state diffusion of Ni–Ti and Ni–TiH$_2$ under CaH$_2$ reducing environment

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Hafizah Hanim Mohd Zaki *, Jamaluddin Abdullah

School of Mechanical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia

ABSTRACT

Phase formation of NiTi via solid state diffusion from Ni–Ti and Ni–TiH$_2$ powders under a CaH$_2$ reducing environment were investigated. Elemental powder sintering of Ni–Ti at equiatomic composition did not result in single phase TiNi, but rather in multi-phases, including Ti$_2$Ni, TiNi, and TiNi$_3$. In this work, we show evidence that powder sintering of Ni–TiH$_2$ produces single phase NiTi with good transformation heat both on cooling and heating with $\Delta H_{A-M} = 26.04$ J/g and $\Delta H_{M-A} = 25.53$ J/g, respectively. The use of CaH$_2$ as the in situ reducing agent and of TiH$_2$ to replace Ti as the starting powder, protected the sample successfully from oxidation.

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1. Introduction

Among other shape memory alloys, the alloy NiTi has received much interest with regard potential use in various applications, such as actuators [1,2], sensors [1], smart tools [1], medicine [1,3], and in consumer goods as functional material [1]. Recently, with the increasing demand for improved functionality of these materials, attention has been given to creating novel structured NiTi alloys, e.g., porous NiTi [4,5], thin film NiTi [6,7], multilayer NiTi and functional gradient NiTi [8,9].

Porous NiTi is of special interest for a range of innovative engineering applications, the most acclaimed being in medical applications for bone implants due to its unique superelasticity that enables the monolithic NiTi to recover up to 8% strain in uniaxial deformation [3] compared with ~0.5% for some stainless steels and surgical alloys. Biologically, the porous structure permits the ingrowth of new bone tissue and thus, it anchors the prosthesis to the surrounding bones [10]. Thus, by engineering NiTi into porous structures, these favorable properties can be tailored to suit better requirements of the application.

Most literature reports that the formation of single phase TiNi via elemental powder sintering has not yet been achieved. Multiple phases, including Ti$_2$Ni, TiNi, and TiNi$_3$, always result from powder synthesis [11–14]. Once formed, these intermetallic phases are difficult to remove, even after post treatment, because they are thermodynamically stable [15]. The main obstacle to producing single phase NiTi is

the oxidation problem. Although the sintering is conducted under argon protection, the preservation of a fully non-oxidizing environment is still not guaranteed owing to the limitations of the equipment. Ti is oxidized easily to form TiO$_2$ at the surface owing to its higher affinity to oxygen. Another difficulty is the formation of Ti$_4$Ni$_2$O$_x$ $(0 < x \leq 1)$, which appears and is always misinterpreted as Ti$_2$Ni because of the structure similarity between the two phases [16]. The formation of these two oxides may reduce the Ti content for the Ni–Ti reaction; thus, leaving an abundance of Ni that reacts with Ti to form TiNi$_3$, another unwanted intermetallic phase.

Therefore, this research aims to investigate the conditions that may produce single phase NiTi under solid state by suppressing the oxide levels using CaH$_2$ as reducing agent with elemental Ni and Ti or TiH$_2$.

2. Experimental procedure

Ni (average particle size < 30 μm) and Ti (average particle size < 50 μm) or TiH$_2$ (mean particle size = 44 μm) powders were used in this study. These powders were mixed at equiatomic composition (Ni:Ti and Ni:TiH$_2$) by means of low energy ball milling for 24 h. After mixing, the powder mixture was cold compacted into cylindrical shapes of ϕ12 × 4 mm to 3 Torr. Then, the samples were sintered under flowing argon and a reducing gas environment coupled with CaH$_2$ as the in situ reducing agent to prevent oxidation. For optimal content of CaH$_2$, approximately 200 to 300 mg of CaH$_2$ was poured onto the exposed surface of green compact. Microstructural analyses were examined using a Hitachi scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) was conducted for phase identification. Phase transformation behavior was studied by differential scanning calorimetric (DSC)

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* Corresponding author. Tel.: +60108105094.
E-mail addresses: arename82@gmail.com (H.H. Mohd Zaki),
mejamal@eng.usm.my (J. Abdullah).

measurement using a TA Q10 DSC machine at a heating/cooling rate of 10 K/min.

3. Results and discussion

Fig. 1 shows SEM micrographs of Ni–Ti and Ni–TiH$_2$ sintered at 1203 K for 3 h under a reducing environment with CaH$_2$. The temperature chosen is well below the eutectic point at 1215 K, to avoid partial melting and to ensure solid state reaction during sintering. For diffusion of Ni–Ti, as in Fig. 1(a1), the sample exhibited multiple phases of Ti(Ni), Ti$_2$Ni or Ti$_4$Ni$_2$O$_x$, TiNi, TiNi$_3$ and Ni(Ti), with NiTi being the major phase with average EDS composition of ~52.4 at% Ni (Fig. 1(a2)). Meanwhile, for Ni–TiH$_2$, a single phase NiTi microstructure was observed as shown in Fig. 1(b1). The enlarged view, in Fig. 1(b2) confirms no other phase forms, except NiTi with an average EDS composition of ~48.8 at% Ni.

Comparing Fig. 1(a) and (b), the use of TiH$_2$ to replace Ti, coupled with the presence of CaH$_2$, diminishes drastically the unwanted intermetallic phases, such as TiNi$_3$ and Ti$_2$Ni or Ti$_4$Ni$_2$O$_x$. The use of CaH$_2$ as the in situ reducing agent only protect the sample from oxidation once Ca becomes available at its decomposition temperature of ~1073 K. According to Eq. (1), Ti is oxidized easily to form TiO$_2$ at the surface even at low temperature owing to its higher affinity. Therefore, TiH$_2$ was used as the starting powder to replace Ti, as oxidation protection at lower temperatures. TiH$_2$ decomposes at 673 K according to Eq. (2). The formation of TiO$_2$ depletes Ti content for Ni–Ti reaction, leaving abundance of Ni that reacts with remaining Ti to form TiNi$_3$ as in Eq. (3).

$$Ti + O_2 \rightarrow TiO_2 \tag{1}$$

$$TiH_2 \rightarrow Ti + H_2 \tag{2}$$

$$3Ni + Ti \rightarrow Ni_3Ti \tag{3}$$

While TiH$_2$ replenishes fresh Ti into the system for further Ni–Ti reaction, depletion of oxygen in the environment by CaH$_2$ further safeguard the TiNi from oxidation, thus preventing Ti$_4$Ni$_2$O$_x$ formation.

Fig. 2 shows the XRD spectra of Ni–Ti and Ni–TiH$_2$ powder mixtures and samples sintered at 1203 K for 3 h. The Ni–Ti and Ni–TiH$_2$ powder mixtures showed only elemental Ni and Ti, and Ni and TiH$_2$, respectively. For Ni–Ti sample, B2-NiTi is the dominant phase with Ti$_2$Ni and TiNi$_3$ being the next two major presences in the microstructure. Some residual Ni is still visible, whereas no Ti is observed in the XRD spectrum, However, the EDS confirms the presence of Ti in the sample. This is due to the limitation of XRD in detecting phases of low volume fractions. Meanwhile, for the Ni–TiH$_2$ sample, only NiTi peaks associated with B2 and B19′ were detected. The highest intensity peaks correspond to B2-NiTi due to its major stable phase at room temperature.

The transformation behaviors of the Ni–Ti and Ni–TiH$_2$ samples are shown in Fig. 3. For the Ni–Ti sample, no transformation peak was detected. This is attributed to the low volume fraction of the B2-NiTi phase, and also the high Ni content in the NiTi matrix, which falls in the range of 52–54 at%. It is known that B2–B19′ martensitic transformation temperatures are dependent highly on the Ni content in NiTi. With increasing Ni content in the B2-phase, the transformation temperatures decrease rapidly and drop to 0 K at Ni=51.7 at% [17].

Meanwhile for Ni–TiH$_2$, the sample displays A→M (cooling) and M→A (heating) transformation with enthalphy change of ΔH_{A-M}= 26.04 J/g and ΔH_{M-A}=25.53 J/g, respectively, in agreement with the values usually found in melt cast Ti-rich alloy [18]. The two overlapping peaks phenomenon (referred to as A$_{p1}$ and A$_{p2}$) observed upon heating is not attributed to the R-phase, it is instead
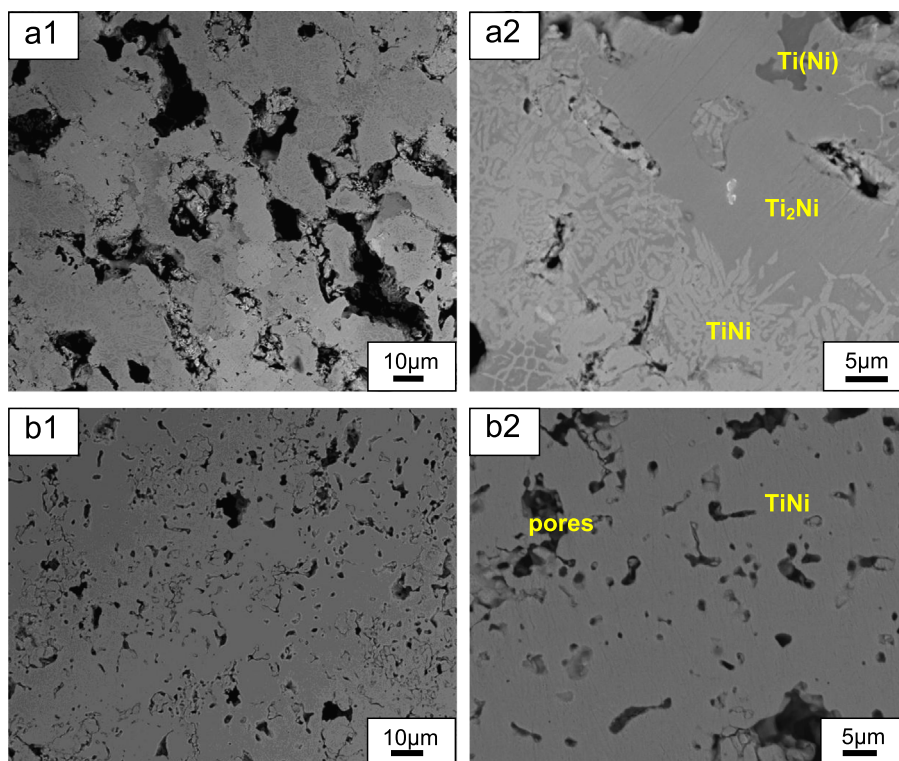

Fig. 1. SEM with backscattered image of sample: (a) Ni–Ti, (b) Ni–TiH$_2$, sintered at 1203 K for 3 h.