Enhanced mechanical properties of spark plasma sintered NiTi composites reinforced with carbon nanotubes

Junho Lee\sa, Jaewon Hwang\sa, Dongju Lee\sa, Ho Jin Ryu\sa,\sb, Soon Hyung Hong\sa,\sc

\sa Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea
\sb Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

Abstract

To enhance the mechanical strength of NiTi, 0.5 vol% CNT/NiTi composite was fabricated by high-energy ball milling followed by spark plasma sintering. NiTi and 1 vol% TiC/NiTi composites were also fabricated using the same process for comparison. Unreacted CNTs were observed in the CNT/NiTi composites, although some CNTs had reacted with Ti to form a TiC phase. Thermal hysteresis increased with the addition of CNTs due to increased frictional resistance to interfacial motion between CNT and NiTi matrix, and relaxation of the elastic strain energy in the NiTi matrix. The addition of CNTs, however, had little influence on the shape memory effect of NiTi. The elastic modulus, yield strength and ultimate tensile strength of the 0.5 vol% CNT/NiTi composite were greater than that of the NiTi. This improvement was attributed to the effective load transfer to the unreacted CNTs.

1. Introduction

Shape memory alloys (SMAs) have unique properties, including shape memory and superelasticity due to a phase transformation between the martensite and austenite phases. When compared with Cu- and Fe-based SMAs, NiTi SMAs are highly corrosion resistant and possess a superior shape memory effect. NiTi SMAs that are subjected to strain of up to 8% can be returned back to its original shape by heating\cite{1}. Consequently, NiTi SMAs can be used in tribological, pipe coupling, and seismic applications. However, the low mechanical strength and elastic modulus of NiTi SMAs are major obstacles to broadening their applications.

Numerous attempts have been made to improve the tensile properties, compressive properties, and wear resistance of NiTi SMAs. Reinforcement of the NiTi matrix by TiC, TiN, or SiC has resulted in higher yield strengths and improved wear resistance, but decreased fracture strain to about 4% such that the shape memory effect could not be characterized\cite{2–4}. It is generally thought that external loads are sustained by hard reinforcements, and thus the mechanical strength of NiTi SMAs is major obstacles to broadening their applications.

In this paper, we describe the preparation of CNT-reinforced NiTi matrix composites through a powder metallurgical process using CNTs, and Ni and Ti elemental powders. Spark plasma sintering (SPS), which requires a very short time to sinter metal and ceramic powders, was applied to consolidate the CNT/NiTi composite powder. The effect of the CNTs on the mechanical properties of the composites was investigated. TiC/NiTi composites were also...
fabricated using the same process in order to directly compare their mechanical properties with those of the CNT/NiTi composites.

2. Experimental

Nickel powder (Kojundo, ca. 2–3-μm particle diameter), titanium powder (Kojundo, particle diameter less than 38 μm), CNT powder (Hanwha Nanotech, diameter 10–20 nm and length 10–20 μm), and titanium carbide powder (H.C. Starck, particle diameter less than 5 μm) were used as the starting materials. The microstructures of the raw materials are shown in Fig. 1. The Ni and Ti powders, and the CNTs were processed in a planetary ball mill (Fritsch GmbH, Pulverisette 5) for 2 h at a rotation speed of 100 rpm and a 12:1 ball-to-powder ratio in an Ar atmosphere to produce a CNT/NiTi composite powder. The matrix composition and volume fraction of CNT were designed as 50:50 (Ni:Ti) at.% and 0.5 vol%, respectively. Steel balls with a diameter of 8 mm were used for high-energy ball milling. The as-milled powders were consolidated by spark plasma sintering at 900 °C for 5 min at a pressure of 50 MPa in a vacuum of 10 Pa. The heating rate up to the sintering temperature was 100 °C/min. After consolidation, the samples were homogenized at 1050 °C for 12 h. For comparison, NiTi and 1.0 vol% TiC/NiTi composite were produced using the same fabrication process. Note that 0.5 vol% CNT can form 1.0 vol% TiC if a complete reaction of CNTs with Ti takes place. The volume fraction of reinforcements for each sample refers to the original amount of reinforcement powders added to the sample.

The microstructures of the powders and solution-treated specimens were examined by high-resolution scanning electron microscopy (SEM, Hitachi S-4800) equipped with an energy-dispersive spectrometer (EDS). The specimens were etched in a 1:1:8 solution of HF:HNO3:glycerine prior to microstructure observations. Phase identification in the specimens was performed using an X-ray diffractometer (XRD, Rigaku D/MAX-IIIC). Phase transformation behavior was observed by differential scanning calorimetry (DSC) in a TA Q20 DSC instrument at a heating/cooling rate of 10 K/min in a N2 atmosphere. Tensile tests were disentangled by the high impact energy of the balls during the milling process. Fig. 2(c) shows the morphology of the 1.0 vol% TiC/NiTi composite powder. It was assumed that the TiC particles were uniformly dispersed in the 1.0 vol% TiC/NiTi composite, although discrete TiC particles were not observed since they were embedded in the mechanically alloyed Ni and Ti powders.

Fig. 3 shows the microstructure and the EDS spectra of the NiTi, and the 0.5 vol% CNT/NiTi and 1.0 vol% TiC/NiTi composites. EDS was used to determine the elemental composition of the different regions in the sample. The SEM micrographs in Fig. 3 show a dark phase (black circle) that corresponds to the NiTi matrix phase, and a lighter phase (red circle) that corresponds to Ti2Ni, which exists mainly at the grain boundary [16]. The grain sizes of the NiTi and the composites are summarized in Table 1. In general, the yield strength of polycrystalline metals depends on the grain size. This is known as the Hall–Petch relationship. Table 1 shows that the grain size of NiTi was almost the same as that of the 0.5 vol% CNT/NiTi and 1.0 vol% TiC/NiTi composites. This indicates that strengthening by grain refinement with the addition of reinforcements was not significant in the 0.5 vol% CNT/NiTi and 1.0 vol% TiC/NiTi composites.

XRD patterns of the NiTi, and the 0.5 vol% CNT/NiTi and 1.0 vol% TiC/NiTi composites are shown in Fig. 4. Note that the phases in the NiTi and the composites included NiTi (B2), NiTi (B19′), and Ti2Ni. The Ti2Ni phase was formed during the sintering process in all of the samples because it is thermodynamically favorable phase at the sintering temperature compared than NiTi phase [17]:

\[
Ni + Ti \rightarrow NiTi, \quad \Delta G = -176.7 kJ/mol \text{ at } 1173 K
\]  
\[
Ni + 2Ti \rightarrow Ti2Ni, \quad \Delta G = -251.4 kJ/mol \text{ at } 1173 K
\]

In addition, diffraction peaks corresponding to a TiC phase appeared in the XRD patterns of the 0.5 vol% CNT/NiTi and 1.0 vol% TiC/NiTi composites. The formation of TiC in the 0.5 vol% CNT/NiTi composite originated from the reaction of CNTs with Ti. The following equation describes the Gibbs free energy of TiC formation [18]:

Fig. 1. SEM images of raw materials (a) Ni powder, (b) Ti powder, (c) CNT powder and (d) TiC powder.
Fig. 2. SEM micrographs of as-milled (a) NiTi powder, (b) 0.5 vol% CNT/NiTi composite powder and (c) 1.0 vol% TiC/NiTi composite powder with insets of low magnification micrographs.

Table 1
Grain size of the NiTi, and the CNT/NiTi and TiC/NiTi composites.

<table>
<thead>
<tr>
<th></th>
<th>NiTi</th>
<th>0.5 vol% CNT/NiTi</th>
<th>1.0 vol% TiC/NiTi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (μm)</td>
<td>43.34 ± 18.78</td>
<td>44.04 ± 8.88</td>
<td>48.09 ± 20.93</td>
</tr>
</tbody>
</table>

Fig. 3. Microstructural and EDS elemental analyses of the various regions of the (a) NiTi, and the (b) 0.5 vol% CNT/NiTi and (c) 1.0 vol% TiC/NiTi composites. Red circles for lighter phase and black circles for dark phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. XRD patterns of the NiTi, the CNT/NiTi and TiC/NiTi composites.

Fig. 5. SEM micrograph showing unreacted CNT on etched surface of the 0.5 vol% CNT/NiTi composite.
The $\Delta G$ for the reaction between the Ti and CNTs at 1173 K is approximately $-175$ kJ/mol, which shows that TiC formation is spontaneous during spark plasma sintering. The formation of TiC by the reaction of CNTs or carbon black with Ti has been reported in previous studies [14,19,20]. However, some CNTs remained unreacted, with a cylindrical morphology and an approximate 20-nm diameter, and can be seen on the etched surface of the 0.5 vol% CNT/NiTi composite in Fig. 5. This is probably because the basal plane of graphite is stable with regard to Ti during the sintering process and solution treatment [21].

Fig. 6 shows DSC curves of the (a) NiTi, (b) 0.5 vol% CNT/NiTi and (c) 1.0 vol% TiC/NiTi composites. Fig. 7 shows shape memory tests performed by sequential loading and unloading of the (a) NiTi, (b) 0.5 vol% CNT/NiTi and (c) 1.0 vol% TiC/NiTi composites. Phase transformations occurred in the NiTi and in the composites during both cooling and heating, which demonstrates that all of the samples had shape memory.

Table 2

<table>
<thead>
<tr>
<th></th>
<th>$M_f$ (°C)</th>
<th>$M_s$ (°C)</th>
<th>$A_s$ (°C)</th>
<th>$A_f$ (°C)</th>
<th>Hysteresis ($A_f - M_s$) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiTi</td>
<td>43.9</td>
<td>66.9</td>
<td>81.4</td>
<td>106.2</td>
<td>39.3</td>
</tr>
<tr>
<td>0.5 vol% CNT/NiTi</td>
<td>38.2</td>
<td>63.3</td>
<td>79.8</td>
<td>105.5</td>
<td>42.2</td>
</tr>
<tr>
<td>1.0 vol% TiC/NiTi</td>
<td>44.6</td>
<td>68</td>
<td>83</td>
<td>121.2</td>
<td>53.2</td>
</tr>
</tbody>
</table>
In Fig. 6, only one phase transformation peak could be observed in all of the DSC curves of the samples during cooling and heating, corresponding to B2 → B19 and B19 → B2, respectively. The phase transformation temperatures and thermal hysteresis of the NiTi and the composites are listed in Table 2. Note that thermal hysteresis is defined as the difference between the austenitic finish temperature (Af) and the martensitic start temperature (Ms) [22]. With the addition of CNTs into the NiTi, the phase transformation temperatures decreased due to the reaction between the CNTs and Ti. This result agrees with those of previous studies [22–24], which have shown that phase transformation temperatures decrease as the Ni/Ti ratio increases. Thermal hysteresis in the 0.5 vol% CNT/NiTi composite was greater than that in the NiTi. Likewise, the addition of 1.0 vol% TiC to the NiTi matrix increased the thermal hysteresis. It is generally thought that the addition of hard reinforcements to a NiTi matrix enlarges thermal hysteresis due to increased frictional resistance to interfacial motion between B19′ and B2 in the NiTi matrix. In addition, lattice mismatch between the reinforcements and the NiTi matrix relaxes the elastic strain energy, which is the driving force for the reverse phase transformation (B19′ → B2) [25]. Thus, the thermal hysteresis measurements indicated that the phase transformation of the 0.5 vol% CNT/NiTi composite was less affected by the CNT reinforcements than that of the 1.0 vol% TiC/NiTi composite.

Shape recovery tests were performed by sequentially loading and unloading the NiTi, and the 0.5 vol% CNT/NiTi and 1.0 vol% TiC/NiTi composites during tensile tests under Mt, followed by heating to above At. The results of these shape memory tests are presented in Fig. 7. The NiTi exhibited perfect shape recovery following a 3.5% deformation, although commercial NiTi SMAs produced by melting process generally show 100% shape recovery following a 6% strain. This is probably because Ti2Ni phase as well as NiTi phase was formed in the fabrication process, and thus NiTi phase having shape memory effect was not maximized. After heating, a shape recovery of 68.9% was observed after a strain of 6.56%. This decrease in the shape recovery ratio originated from permanent deformation as the strain was increased from 3.5% to 6.56%. The 0.5 vol% CNT/NiTi composite experienced a 94% shape recovery after heating following a deformation of 3.7%. The recovery was 67.8% after a strain of 6.21%. In the 1.0 vol% TiC/NiTi composite, recoveries of 87.5% and 71% were measured following strains of 3.36% and 6.7%, respectively. When 0.5 vol% CNT was added to the NiTi matrix, the shape memory effect was less degraded than when 1.0 vol% TiC was added. This shows that the 0.5 vol% CNT had a weaker effect on reverse phase transformations from B19′ to B2 than did the 1.0 vol% TiC. This is in agreement with the wider interval between the reverse transformation temperatures (Af – At) of 1.0 vol% TiC/NiTi composite than that of 0.5 vol% CNT/NiTi composite as shown in Fig. 6.

Table 3
Mechanical properties of the NiTi and the CNT/NiTi and TiC/NiTi composites.

<table>
<thead>
<tr>
<th></th>
<th>Elastic modulus (GPa)</th>
<th>Yield strength (MPa)</th>
<th>Ultimate tensile strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiTi</td>
<td>61</td>
<td>151</td>
<td>876</td>
<td>11.2</td>
</tr>
<tr>
<td>0.5 vol% CNT/NiTi</td>
<td>79 (29%)</td>
<td>192 (27%)</td>
<td>975 (11%)</td>
<td>9.4 (16%)</td>
</tr>
<tr>
<td>1.0 vol% TiC/NiTi</td>
<td>77 (26%)</td>
<td>177 (17%)</td>
<td>891 (1.7%)</td>
<td>8.2 (26%)</td>
</tr>
</tbody>
</table>

Fig. 8 shows stress–strain curves of the NiTi, and the 0.5 vol% CNT/NiTi and 1.0 vol% TiC/NiTi composites under Mt. All of the samples showed typical stress–strain curves of a shape memory alloy, with double yield points on the curve [26]. Typical stress–strain curves of shape memory alloys can be separated into four regions [27]. The martensite twins begin to reorient and is detwinned at the first yield point followed by elastic region of martensite of NiTi. This reorientation continues in the first plateau. Subsequently, fully detwinned martensite is deformed elastically up to the second yield point, with plastic deformation occurring in the second plateau. The yield strength, elastic modulus, and ultimate tensile strength of the NiTi, and the 0.5 vol% CNT/NiTi and 1.0 vol% TiC/NiTi composites, as determined from the stress–strain curves, are summarized in Table 3. The yield strength of the 0.5 vol% CNT/NiTi and the 1.0 vol% TiC/NiTi composites increased by 29% and 26%, respectively, relative to that of the NiTi. The CNTs and TiC present in the NiTi matrix constrained the reorientation of martensite twins, and thus enhanced the yield strength. The addition of CNTs also raised the tensile strength by 11%. The tensile strength of the 1.0 vol% TiC/NiTi composite was slightly higher.

Fig. 9. CNTs observed at the fracture surface of the 0.5 vol% CNT/NiTi composite; (a) low magnification and (b) high magnification.
than that of the NiTi. Note that small additions of CNTs to the NiTi matrix resulted in a greater enhancement in the mechanical properties, including improved strength and minimally reduced elongation, than did the addition of TiC. This was due to the presence of unreacted CNTs in the NiTi matrix, as seen in the fracture surface of the CNT/NiTi composite in Fig. 9. Also, slope of second elastic region of the 0.5 vol% CNT/NiTi composite is larger than that of NiTi in Fig. 8, which shows that effective load transfer from the NiTi matrix to the reinforcements occurs. This demonstrates that CNTs may be used as a reinforcement material with minimal impact on the intrinsic properties of a NiTi matrix.

4. Conclusions

CNT/NiTi composites mixed with 0.5 vol% CNTs were prepared by high-energy ball milling followed by a powder metallurgical process in an effort to improve the mechanical strength of NiTi. For comparison, an NiTi alloy and a TiC/NiTi composite containing 1.0 vol% TiC were also prepared using the same fabrication process. The shape memory behavior of the 0.5 vol% CNT/NiTi composite was only slightly degraded relative to the NiTi while the shape memory effects was further degraded in the 1.0 vol% TiC/NiTi composite relative to the 0.5 vol% CNT/NiTi composite. The elastic modulus, yield strength and ultimate tensile strength of the 0.5 vol% CNT/NiTi composite was greater than that of the NiTi or the 1.0 vol% TiC/NiTi composite. Relatively small additions of CNTs had little influence on the shape memory effects of the NiTi while improving the mechanical strength due to the presence of unreacted CNTs in the NiTi matrix.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2009-0094038) and AOAD through Contract No. 114008.