

Synthesis of TiC/NiTi composite powders in molten salt and their sintering

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Received: 9 January 2007 / Accepted: 6 September 2007 / Published online: 26 September 2007
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Abstract In this paper, TiC/NiTi composite powders were prepared by putting Ni, Ti and C powders into a molten salt bath. The as-prepared composite powders were then sintered by a cubic high-pressure apparatus to produce bulk composite materials at a very short time. It was found that the composite was composed of TiC particles embedded in NiTi matrix, in which a small amount of Ti₂Ni was also detected. The martensitic transformation of the NiTi matrix was evidenced by differential scanning calorimetry analysis.

Introduction

Shape memory alloys (SMAs) have been the subject of active research for over four decades due to their unique attributes and the resulting potential applications [1]. Compared with other SMAs, NiTi alloys are the most important because of their excellent properties [2]. Consequently, NiTi alloys are expected to be used in many engineering applications, including active, adaptive or smart structures, shape memory composites, biomedical purposes [3, 4], pipe couplings, electronic connectors and others [5]. Recently, studies and development of hard particles reinforced NiTi composites have seen significant growth because these NiTi composites possess both actuating functions and wear-resistance which lead to many potential applications [6–8]. Many studies have shown that

TiC/NiTi composites have significant potentiality for wear resistance [9, 10].

Previous works on the TiC/NiTi composites have primarily focused on the characterization of the properties of composites which were prepared by conventional powder processing techniques. These techniques are listed in Table 1. Most of these methods require high cost equipment and long processing time, which are necessary to drive the conversion complete from reactants to products. Moreover, the previous researches did not pay much attention on the martensitic transformation of the NiTi in the TiC/NiTi composites, or the reverse martensitic transformation of the NiTi matrix has not even been mentioned in some researches [10, 20].

In this research, the TiC/NiTi composite powders were produced by in situ reaction in the molten salt, and bulk TiC/NiTi composites were produced by a cubic high-pressure apparatus from the as-prepared powders.

Experimental materials and methods

The Ni, Ti and C powders with a size of 70 μm and purity of 99.9% were used as raw materials. The equimolar NaCl (99.5% purity) and KCl (99.5% purity) mixtures were used as the salt medium. It is known that TiC is a nonstoichiometric compound, and the atomic ratio of C/Ti is about 0.48–1. Therefore, Ni, Ti and C powders were mixed in a range from 1:2.5:1 to 1:2.8:1.

The blended Ni–Ti–C powders were loaded into a stainless steel vial with hardened steel balls, with a ball/powder weight ratio of 20:1. The vials were sealed with an O-ring to maintain the internal argon atmosphere. The ball milling process was carried out at room temperature in a planetary ball mill for specified times. A rotational speed of

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Table 1 Conventional methods used to synthesize TiC/NiTi composite

Authors	Methods
Goldstein [11]	Infiltration of porous carbon by a Ti-rich NiTi alloy, followed by heating to provide solid-state conversion of carbon into TiC
Poletika et al. [12, 13]	Sintering of TiC and NiTi powders for 1 h at 1250–1300 °C
Goldstein [14]	A sequence of CIPing at 680 MPa, sealing in a steel container evacuated to less than 100 microns, sintering between 900 and 1195 °C, followed by hot working to reduce the cross sectional by at least 25%
Tabachenko and Krychkova [15]	Ignition of a self-propagating high-temperature reaction of element Ti, Ni and C powders
Mari and Dunand [16]	Vacuum hot pressing of NiTi and TiC powders for 3.5 h at 1150 °C and 25 MPa
Fukami and Dunand [17]	Vacuum hot pressing of NiTi and TiC powders for 4–6 h at 1080 °C and 65–75 MPa, followed by HIPing for 2 h at 1160 °C and 172 MPa
Huang et al. [18]	Ball mill of element Ti, Ni and C powders for 3 h and 35 min
Vaidyanathan et al. [19]	HIPing of NiTi and TiC powders for 3 h at 1065 °C and 100 MPa
Ye et al. [6]	Cold pressing Ti, Ni and TiC powders at 787 MPa for 30 s, followed by sintering at 900–1500 °C for 6 h
Burkes et al. [20]	Combustion synthesis of Ti, Ni and C powders coupled with a quasi-isostatic densification

300 rev/min was selected. After the ball milling process, equimolar NaCl and KCl powder mixtures (60 wt.%) were added into the mixed Ni–Ti–C powders. Then the resultant powders (Ni–Ti–C–NaCl–KCl) were cold-pressed into pellets of 3 mm in thickness, 5 mm in diameter.

A quartz crucible was used as the container of the salt bath. The pellets were dropped into the molten salt at 800 °C and held for 30 min. After the crucible cooled down to the room temperature, the product powders (TiC/NiTi) were separated by washing with distilled water.

The as-prepared TiC/NiTi powders were cold pressed into cylindrical bars ($\Phi 14 \times 10$ mm) under a pressure of 4 MPa. The bars were sintered by a cubic high-pressure apparatus at 1,000 °C for 10 min with graphite die ($\Phi 14 \times 10$ mm). The pressure applied was 8 GPa.

A 204F1 differential scanning calorimeter (DSC) was used to study the martensitic transformation of the NiTi with a heating and cooling speed of 10 °C/min. X-ray diffraction (XRD) analyses were conducted using a Rigaku DMAX-RB X-ray diffractometer (Cu–K α radiation, $\lambda = 0.154$ nm). The microstructure of the end-product was observed using a Cambridge S-360 scanning electron microscope (SEM).

Results and discussion

The XRD patterns of the end-product before and after sintering are shown in Fig. 1. The patterns show that this sample was composed of TiC, NiTi and a trace amount of Ti₂Ni. Obviously, Ti reacted with C, which produced TiC,

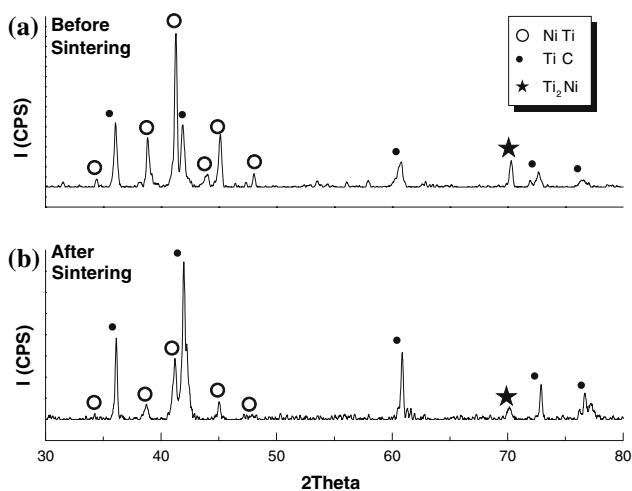


Fig. 1 The X-ray diffraction patterns of the TiC/NiTi composite before and after sintering. (a) The end-product powders after reaction in molten salt (800 °C, 30 min); (b) the end-product after sintering in cubic high pressure apparatus (1,000 °C, 10 min, 8 GPa)

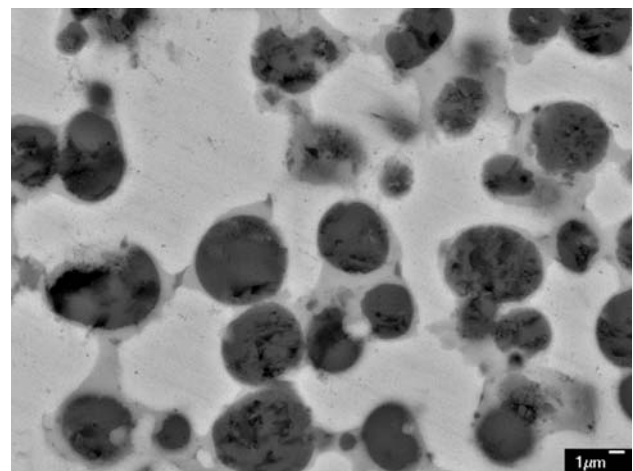
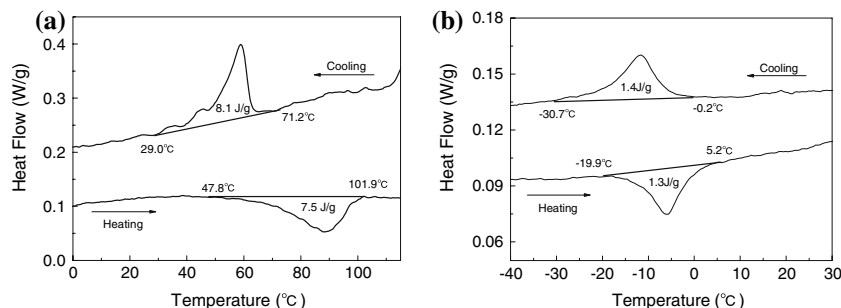


Fig. 2 The backscatter electron images of the TiC/NiTi composite after sintering

Fig. 3 The DSC curves of TiC/NiTi composite powders before and after sintering. (a) The end-product powders after reaction in molten salt (800 °C, 30 min); (b) the end-product after sintering in cubic high pressure apparatus (1,000 °C, 10 min, 8 GPa)



and with Ni, which produced NiTi and Ti₂Ni in the molten salt. According to the phase diagram of Ni–Ti binary system, the Ti₂Ni is a stable phase, so it may be inevitable to avoid the existence of the Ti₂Ni by-products. From the patterns a and b in Fig. 1, one can see that there was an interesting change after sintering. The diffraction intensity of TiC gets stronger while the one of NiTi gets weaker.

Figure 2 shows the SEM micrograph of the sintered TiC/NiTi composite. One can see that the TiC particle size has a wide distribution from 1 to 10 μm. The matrix is NiTi with a small amount of Ti₂Ni, where NiTi shows a white bright color and Ti₂Ni shows a grey color.

The reverse martensitic transformations of the end-product before and after sintering were evidenced by the DSC curves shown in Fig. 3. It is evident that the phase transition enthalpy of NiTi decreased after sintering. Because the TiC and Ti₂Ni have no martensitic transformation, the only contribution to the phase transition enthalpy comes from NiTi. Therefore the decrease of the phase transition enthalpy means the decrease of the amount of NiTi. This conclusion is consistent with the XRD results shown in Fig. 1.

It is well known that the Ni content strongly affects the phase transformation temperatures of NiTi alloy where 0.1 at% increase in Ni content can lower the phase transformation temperatures by about 10 °C [21–23]. Comparing Fig. 3a,b, the phase transformation temperatures get an apparent decrease, which suggests the increase of the Ni content, or in other words the decrease of the Ti content in NiTi after sintering. Considering the increase of TiC in the composite after sintering, it is reasonable to consider that the “extra” carbon reacted with Ti in NiTi and produced TiC. Now the key issue is where the “extra” carbon comes from. Figure 4 shows the SEM micrograph of the sintered TiC/NiTi composite. The white bright matrix is composed of NiTi and Ti₂Ni. The black particle in the center is the “extra” carbon. During the reaction in the molten salts, there was some residual carbon. Then it is clear that in the subsequent sintering, the residual carbon reacted with Ti in the NiTi and produced TiC. That is the reason why TiC increases and NiTi decreases after sintering.

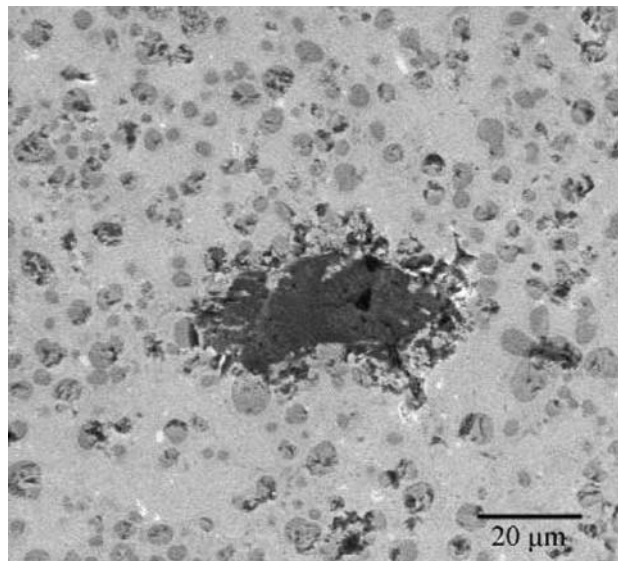


Fig. 4 The SEM photomicrograph of TiC/NiTi composite after sintering

Conclusions

TiC/NiTi composite powders were produced by in situ synthesis in molten salt, and TiC/NiTi composites were sintered by using cubic high-pressure apparatus. The XRD analysis confirmed the existence of NiTi and TiC. The DSC analysis confirmed the presence of the martensitic transformation in the composite. During sintering some residual carbon reacted with Ti in NiTi, which resulted in the increase of TiC and the decrease of NiTi.

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