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Original Research Paper

Fabrication and characterization of NiTi shape memory alloy synthesized by Ni electroless plating of titanium powder

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ABSTRACT

In this work NiTi shape memory alloy was fabricated from mixed elemental powders, Ni plated titanium powder and Ni heated/plated titanium powder by Ar-sintering. Electroless plating process was utilized to fabricate Ni plated titanium powder. For this purpose titanium powder was plated in an electroless Ni bath for 225 min and hydrazine hydrate was used as a reductant to deposit pure nickel on the titanium particles. Ni plated titanium powder was heat treated under an argon atmosphere at 1000 °C to prepare Ni heated/plated titanium powder. Finally, the three sample powders were pressed by CIP followed by sintering at 980 °C for 8 h to manufacture NiTi shape memory alloy. The prepared powders, as well as sintered samples, were characterized by scanning electronic microscopy (SEM), energy dispersive spectrometer analysis (EDS), X-ray fluorescence (XRF), X-ray diffraction (XRD) and differential scanning calorimetric (DSC). The results indicated the presence of NiTi phase and also non-transformable phases ($NiTi_2$ and Ni_3Ti) in the heated/plated Ti powder and sintered samples. NiTi compound was dominated phase in the heated/plated sintered sample. All three sintered samples, as well as heated/plated powder, showed one-step phase transformation (B2 ↔ B19′).

1. Introduction

During the recent decades, NiTi alloys have attracted much interest for their excellent shape memory effects (SME), pseudoelasticity, good mechanical properties, excellent corrosion resistance and biocompatibility [1–4]. These unique properties have made NiTi alloys attractive to use in many applications such as biomedical engineering, smart structures and microelectromechanical systems (MEMS) [5–10]. A number of early studies on such alloys have focused on casting process and issues related to finding the right composition and consolidation temperature. In recent years, however, the focus has shifted towards the study of approaching new ways and methods of powder processing altogether in an attempt to discover convenient and effective ways to manufacture shape memory alloys because not only some problems associated with casting such as segregation or extensive grain growth may be avoided by Powder Metallurgy technique but also this technique allows a precise control on the chemical composition of the alloy and also allows for easier achievement of complex shapes with minimal post-machining treatment. Furthermore, due to the difficulty of the machining of NiTi alloys, either tungsten carbide tool whose lifetime is short should be used or electron discharge machining which is costly should be employed. One way to outreach these problems is the use of near-net shape process by powder metallurgy.

The recent researches have ranged from introducing different PM processes to fabricate shape memory alloys (elemental powder metallurgy (EPM) [3], self-propagating high temperature synthesis (SHS) [4,11] and hot isostatic press (HIP) [12]) to incorporating multiple stages of processing to study sintering behavior, dimensional and density changes as a function of compaction pressure and the effect of temperatures and sintering time [2,3,13–17]. Among implemented PM techniques EPM is one of the stable processing routes for the manufacture of shape memory products with economic incentives but most of the studies on the EPM process have been restricted to the use of mixed Ni-Ti powders [16–18]. The mechanical mixture of Ni and Ti particles makes a reduction in uniformity of the binary powder while electroless plating process can deposit a homogeneous Ni layer on Ti powder particles and consequently more homogenous Ni-Ti binary powder can be prepared in a green compact with an effect in microstructure and thermal behavior of fabricated NiTi shape memory alloy.

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The electroless plating process is one of the most effective and economic techniques for synthesis of metal–metal binary powders as well as ceramic–metal composite ones which can improve sinterability of primary powders during production procedures [19–22]. In this technique, deposition of metal from its ionic states in the solution occurs by reductant rather than by electric current. This method provides a uniform adherent metal layer on powder substrate [23]. Moreover, the electroless plated powders exhibit a high level of homogeneity after PM processes [24]. The electroless plating is controlled by various parameters such as plating time, temperature, powder load, pH and chemical composition of the bath. In our previous works [25,26], the effect of plating time and reductant concentration on the deposition rate as well as surface morphology of plated/coated Ti powder was investigated also preparation of Ni_xTi_y intermetallic powder synthesized by heat treatment of Ni-plated Ti powder was evaluated. This study will particularly help in understanding the contribution of Ni plated Ti powder and Ni heated/plated Ti powder towards microstructural and thermal behavior of fabricated NiTi alloy.

2. Experimental

2.1. Preparation of mixed powder

Commercially pure Ti powders (<45 μm) supplied by Alfa Aesar and Ni powders (<10 μm) supplied by Sigma-Aldrich were used to fabricate Mechanically mixed powder sample in this study. The powders were mixed for 24 h in a rotating mixer at a Ni-Ti atomic ration of 1:1.

2.2. Preparation of plated powder

The same pure Ti powder (<45 μm) was plated by Ni electroless plating process. Pretreatment was carried out in a solution of Ni chloride (30 g L^{-1}), sodium citrate (20 g L^{-1}), ammonium chloride (7 g L^{-1}), and sodium fluoride (0.5 g L^{-1}) for 60 min at room temperature in order to cleaning and activating the surface of Ti particles. The pH of pretreatment bath was adjusted to 8.5–9 using ammonia solution. Distribution of the Ti particles within bath was obtained via stirring the bath solution by a magnetic stirrer. The pretreated Ti powder was separated from the solution, rinsed, and dried in an oven at 50 °C for 30 min. The pretreated powder was added to the electroless Ni bath containing 100 g L^{-1} Ni chloride and 80 ml L^{-1} hydrazine hydrate (with 80% concentration). The temperature of 85 °C–90 °C was maintained throughout the experiment and pH value of the electroless bath was kept at 9–10 by the addition of ammonia solution to the bath. Plating time was selected 225 min to obtain an atomic ratio of 1:1 for Ni–Ti binary powder. After plating, powders were removed from the bath, rinsed with distilled water and dried in an oven at a temperature of 50 °C for 30 min.

2.3. Preparation of heated/plated powder

Heat treatment of the Ni-coated Titanium powder was conducted at 1000 °C with a heating rate of 10 °C/min in an argon gas-protected furnace for 1 h. The heated/plated powder was further homogenized at 1000 °C for another 4 h.

2.4. Sintering process

Mechanically mixed powder, Ni plated Ti powder and Ni heated/plated Ti powder compacted by cold isostatic press (CIP) under a pressure of 200 MPa to fabricate S_1, S_2 and S_3 samples respectively (Table 1). The L/d ratio (where L is the length and d is the diameter) of the green compact was about 0.7. Sintering was carried out at 980 °C for 8 h in a tube furnace under high-purity (99.999%) argon atmosphere. For this purpose, compacted powders were heated to 700 °C with a heating rate of 10 °C/min and then heated to 980 °C with a heating rate of 5 °C/min and finally the samples were furnace cooled. The green density was calculated directly from the size and weight of the compacts, while the sintered density was determined by the Archimedes method.

Table 1
Utilized powders for fabrication of sintered samples.

Symbol	Sample description
S_1	Mechanically mixed powder
S_2	Nickel plated titanium powder
S_3	Nickel heated/plated titanium powder

The sintered samples were progressively mechanical polished with 400–1000 grit waterproof emery paper and then etched in a fresh solution of 5%HF-5%HNO3. The composition of the prepared powders was detected using energy dispersive spectroscopy (EDS) and X-ray fluorescence (XRF) methods. VEGA\\TESCAN-XMU scanning electron microscope (SEM) was used to analyze the microstructure of the sintered samples and the particle morphology of the initial and prepared powders. The crystal phases in the heated/plated powder, as well as sintered samples, were identified using a PW1800- PHILIPS model X-ray diffractometer (XRD), using Cu Kα radiation (k ¼0.154 nm). The martensitic transformation temperatures of the heated/plated powder and the sintered samples were detected using a TA Q100 differential scanning calorimeter (DSC).

3. Results and discussion

3.1. Mixed powder

Fig. 1 represents the surface morphology of initial and mixed powders. The shape of Ti powder is basically non-spherical (Fig. 1a), which is related to the mechanical milling process used in the production process of powder. Ni powder has irregular clustered morphology (Fig. 1b). As can be seen, there is no bond between Ni and Ti powder particles and Just weak attachments between mixed powder particles were achieved by mixing process (Fig. 1c,d).

3.2. Plated powder

SEM/EDS results of the powder plated for 225 min are illustrated in Fig. 2. The cauliflower-shaped morphology can be observed in the plated powder. This morphology forms when nitrogen gas releases in the electroless bath, according to the following reaction:

$$N_2H_4 + 4OH^- + Ni^{2+} \rightarrow Ni + N2 + 4H_2O + 2e^- \qquad (1)$$

The growth of the Ni crystals is perpendicular to the surface of the Ti particles (in the direction of released gas). Thus, the Ni layer cannot laterally grow on the powder particles, and consequently, a cauliflower-shaped morphology is formed. From the EDS data atomic percentage of deposited Ni on the surface of the Ti particles is 64.29%. Further studies by XRF analysis confirmed an atomic ratio of 50.5–49.5 for Ni-Ti.

3.3. Heated/plated powder

Fig. 3a,b shows the SEM micrograph of heated/plated powder while EDS data is presented in Fig. 3c. According to EDS results,

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