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Shape memory TiNi powders produced by plasma rotating electrode process for additive manufacturing

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Abstract: This study aimed to produce spherical TiNi powders suitable for additive manufacturing by plasma rotating electrode process (PREP). Scanning electron microscopy, X-ray diffractometry and differential scanning calorimetry were used to investigate the surface and inner micro-morphology, phase constituent and martensitic transformation temperature of the surface and inner of the atomized TiNi powders with different particle sizes. The results show that the powder surface becomes smoother and the grain becomes finer gradually with decreasing particle size. All the powders exhibit a main *B*2-TiNi phase, while large powders with the particle size ≥178 μm contain additional minor Ti_2Ni and Ni_3Ti secondary phases. These secondary phases are a result of the eutectoid decomposition during cooling. Particles with different particle sizes have experienced different cooling rates during atomization. Various cooling rates cause different martensitic transformation temperatures and routes of the TiNi powders; in particular, the transformation temperature decreases with decreasing particle size.

Key words: atomization; plasma rotating electrode process; TiNi; particle size; martensitic transformation

1 Introduction

The equiatomic TiNi shape memory alloy was first discovered by BUEHLER et al [1] accidentally. Since its discovery, TiNi alloy has been attracting continuous research interest due to its unique properties such as shape memory effect, good corrosion resistance and good biocompatibility [2]. Recently, additive manufacturing (AM) such as selective laser melting (SLM) process, has been used to fabricate TiNi products for medical implants or actuators [3−8]. In the SLM process, spherical TiNi powders produced by gas atomization were used as the raw feedstock. Since SLM involves very high localized temperature, the characteristics of raw powders play an important role in determining the microstructure and properties of the additively manufactured (AMed) products. For instance, LI et al [8] found that the Ti_2Ni secondary phase originally from the raw TiNi powders retained in the AMed sample after SLM; some defects or pores in the AMed sample are also thought to inherit from the raw powders. YABLOKOVA et al [9] also found that particle size, shape, size distribution and surface properties of the feedstock powders affect the powder flowability and processing conditions for SLM. Therefore, a thorough characterization of the starting TiNi powders in terms of microstructure, particle size and shape, and martensitic transformation temperature provides critical information about the technical operation and the attained AMed

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engineering products.

In addition to gas atomization, plasma rotating electrode process (PREP) is also a widely used technique to produce spherical powders with high sphericity, low porosity and low interstitials [10−13]. In the PREP set-up, the pre-alloyed TiNi ingot is the electrode. An argon plasma arc is used to melt the rapidly rotating TiNi electrode and molten droplets are spun off and then solidified to form spherical particles in flight in the argon atmosphere [12]. In general, PREP is a rapid cooling process and therefore the high temperature phases can be retained to room temperature. The cooling rate in each individual particle is different, depending on its particle size. Therefore, the phase constituents in various particles might be different. For example, BASAK et al [14] found some Ti_2Ni phase nano-particles co-existing with predominant *B*2-TiNi phase in the macro-sized powders. They speculated that the existence of Ti_2Ni is a result of an equilibrium eutectic reaction owing to the low cooling rate. Nevertheless, the clarification of the existence of secondary phases in the PREP NiTi powder is still lacking. On the other hand, if secondary phases do exist, the mechanism by which these secondary phases are formed is not well understood. BASAK et al [14] suggested that a possible correlation exists between particle size and phases presented in the particles. This study therefore aims to clarify such a correlation, using the PREP technique to produce spherical TiNi powders with a wide range of particle size. The objectives of this study are thereby to investigate the effect of particle size on the micro-morphology, phase constituent and martensitic transformation of the PREPed TiNi powders, and to explain the formation of secondary phases, if they are present.

2 Experimental

The pre-alloyed TiNi rods (48.7%Ti−51.3%Ni, mole fraction), 75 mm in diameter and 400 mm in length, were used as the rotating electrode. The oxygen level in the starting TiNi rod is 0.037% (mass fraction). The spherical TiNi powders were subsequently produced using a PREP atomizer (SLPREP-1, Sailong Metal Materials Co., Ltd., China) [13], as shown in Fig. 1. The entire experiment was performed in a high-purity argon atmosphere. The main PREP processing parameters in this study are shown in Table 1.

Afterwards, the powders were sieved into three batches with various particle size ranges, i.e., ≥178 μm

Table 1 Information for PREP processing parameters

Plasma gas	Rotational speed/(r·min^{-1})	DC current/A	Feeding rate/ (mm·min^{-1})
Ar (4N purity)	12000	1100	~1.3

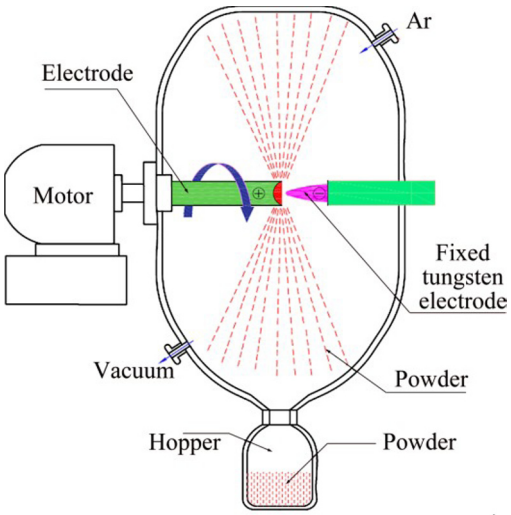

Fig. 1 Schematic of plasma rotating electrode process (PREP)

(denoted by TiNi-Coarse), 74−150 μm (TiNi-Med), ≤40 μm (TiNi-Fine), respectively. The flowability of the PREPed TiNi powders was determined according to the ASTM B213−13 standard with a Hall flowmeter, while their apparent density was determined as per the ASTM B212−13 standard. Phase constituents of the powders were determined by X-ray diffraction (XRD, Bruker D8 Advance Phaser) with Cu K_α radiation at room temperature. The X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance Phaser diffractometer at 40 kV with 2θ angle from 10° to 90°. To prepare the cross-section metallographic samples, the powder particles were mounted in epoxy resin, mechanically polished with SiC papers and finally etched with Kroll's reagent. Scanning electron microscopy (SEM, JEOL JSM−6460) equipped with energy-dispersive X-ray spectrometry (EDX) was used to characterize the surface and cross-sectional microstructures of powders. The interstitial contents were measured with an inert gas fusion analytical instrument (Leco TCH 600). Phase transformation temperatures of the TiNi powders were determined by differential scanning calorimetry (DSC, NETZSCH DSC 204F1) with a heating-and-cooling rate of 10 K/min between −120 and 150 °C.

To investigate the effect of cooling rate on the phase transformation of TiNi during cooling, disk samples of 20 mm in diameter and 5 mm in thickness, cut from the starting TiNi rod were heated to 660 °C, held at this temperature for 0.5 h and then quenched in water. The heating and quenching were conducted in a water-quenching vacuum furnace (vacuum level: 1×10^{-2} Pa). Another experiment was carried out with the same heat profile but followed by furnace cooling instead of water-quenching. In recent work, CHEN et al [15−18]