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Scripta Materialia 52 (2005) 455–460
Scripta MATERIALIA
www.actamat-journals.com

Spark plasma sintering of TiNi nano-powder

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Received 19 August 2004; accepted 12 November 2004

Abstract

Spark plasma sintering of $Ti_{50}Ni_{50}$ nano-powder at a temperature of 800 °C produced specimens showing good shape memory effect and density. Below this temperature, specimens have high porosity but with apparent shape memory effect. By contrast, the specimens sintered at higher temperatures have bulk density, but experienced extensive oxidation with the resulting loss of the shape memory effect.

Keywords: TiNi alloy; Nano-crystalline material; Shape memory alloy (SMA); Differential scanning calorimetry (DSC); Spark plasma sintering

1. Introduction

Titanium–nickel (TiNi) shape memory alloys (SMAs) offer a combination of novel properties, such as the shape memory effect, super-elasticity, biocompatibility and a high damping capacity, which enable them to be widely used in numerous applications, especially for biomedical engineering and microelectromechanical systems (MEMS) [1,2]. These alloys are conventionally produced by arc or induction melting followed by hot or cold working to their final dimensions. However, these processes require multiple remelting to ensure sufficient homogeneity, and have drawbacks of crucible and oxygen contamination as well as difficulty in working or mechanically machining. To produce TiNi components on an industrial scale, near net shape fabrication routes are preferred with limited machining of the alloy.

Recently there has been significant interest in the sintering of TiNi using powder metallurgy (PM) processes [3,4]. This process can avoid the problems associated with casting, like segregation or extensive grain growth [5,6], and has the added advantages of precise control of composition and easy realization of complex part shapes [7,8]. However, the difficulties for the PM process include ease of oxidation, high porosity, low relative density, and tendency to form other Ti–Ni phases, such as Ni_3Ti, Ti_2Ni, Ni_4Ti_3, etc.

Bulk TiNi structures have been fabricated using various PM processes, such as combustion synthesis with self-propagating wave, metal injection molding, hot isostatic pressing (HIP), and spark plasma sintering (SPS) [9–13]. SPS or the field activation method is a relatively new process for powder sintering. Its principle is based on the electrical discharge phenomenon. High energy, low voltage pulsed current momentarily generates extremely high and localized temperatures (up to tens of thousands of degrees) between the powder particles, and causes the surface of the powder particles to vaporize and melt [9]. SPS enables compacted powder to be sintered under uniform heating to high density at relatively lower temperatures, and in a much shorter sintering duration (typically a few minutes) compared to conventional sintering [10]. This shorter sintering time is expected to prevent exaggerated grain growth [11].

Most studies on the PM process of TiNi materials use TiNi powder with micron-sized particles [11–16]. The

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doi:10.1016/j.scriptamat.2004.11.010

refinement of TiNi particles is beneficial for the sintering process [12]. It was reported that the activation energy for nano-size grain growth is higher than that of conventional micron size Al powder and exhibit lower melting and sintering temperatures [13]. However, so far, there are few reports on the preparation of TiNi using nano-size TiNi powder, possibly due to their high surface reactivity and susceptibility to oxygen and carbon contamination.

This study will focus on the characterization of TiNi alloy prepared by SPS of TiNi nano-powder. The nano-powder was prepared by the electroexplosion of wire (EEW) process, in which a continuous wire was fed into a reactor and electro exploded into aerosolized particles that were continuously collected. This process resulted in extraordinary quenching rates producing nano-particles with crystalline and often complex and metastable microstructures [13].

2. Experimental

Nano-TiNi powder (with equiatomic 50/50 nickel/titanium atomic ratio) was prepared using electro-explosion of TiNi wire, in an inert atmosphere of Ar (99.999% purity), by Argonide Nano-materials, USA. The nano-TiNi powder was then sintered using a DR. SINTER™ type SPS 1030 (Sumitomo Coal Mining, Japan). The powder was loaded in a graphite die (13 mm in diameter) and punch unit. The vacuum level of the base chamber was less than 4.5 Pa. The applied compressive pressure level was kept constant at 30 MPa throughout the sintering process. The next step consisted of 30 s pulsed electrical discharge (25 V and 750 A) followed by rapid heating. The actual densification took place during this resistance-sintering step when the high DC current was applied. The sintering temperatures were selected as 700, 800, 900, and 1000 °C with a heating rate of 50 °C/min. After soaking the powder at a desired temperature for 5 min, the applied current was reduced, the pressure released, and the specimen cooled down to room temperature. All of the sintered specimens were then polished to remove any surface carbon contamination.

The microstructures of both the powder and sintered specimens were characterized using a scanning electron microscope (SEM, Hitachi S5300N) and a 200 kV transmission electron microscope (TEM, JEOL JEM-2000EX). Composition was analyzed using an energy dispersive X-ray microanalyzer (EDX). X-ray photoelectron spectroscopy (XPS) analysis was performed on the surface of the polished samples using a Kratos-Axis spectrometer with monochromatic AlKα (1486.71 eV) X-ray radiation and hemispherical analyzer. The survey spectra in the range of 0–1100 eV were recorded in 1 eV step for each sample, followed by high-resolution spectra over different element peaks in 0.1 eV step, from which the detailed composition was calculated. Curve fitting was performed after a Shirley background subtraction by non-linear least square fit using a mixed Gauss/Lorentz function. To remove surface contamination, Ar ion bombardment was carried out for 600 s using a differential pumping ion gun with an accelerating voltage of 4 keV and a gas pressure of 10^{-7} mTorr. The bombardment was performed at an angle of incidence of 45° with respect to the surface normal. The crystalline structures of both the powder and the sintered specimens were obtained using X-ray diffraction (XRD) with CuKα 40 kV/30 mA. The martensitic transformation temperatures were measured by a differential scanning calorimeter (DSC) at a fixed heating/cooling rate of 10 K/min. The density of the sintered NiTi samples was obtained using a technique based on Archimede's principle.

3. Results and discussions

EDX analysis indicates that the powder composition is Ti49.6Ni50.4 at.%. Fig. 1 shows TEM photos of the TiNi nano-powder. The particles are spherical with a fully dense structure. Selected area diffraction of TiNi particles reveals that most of these particles are single crystals in nature. Some particles are martensite, while

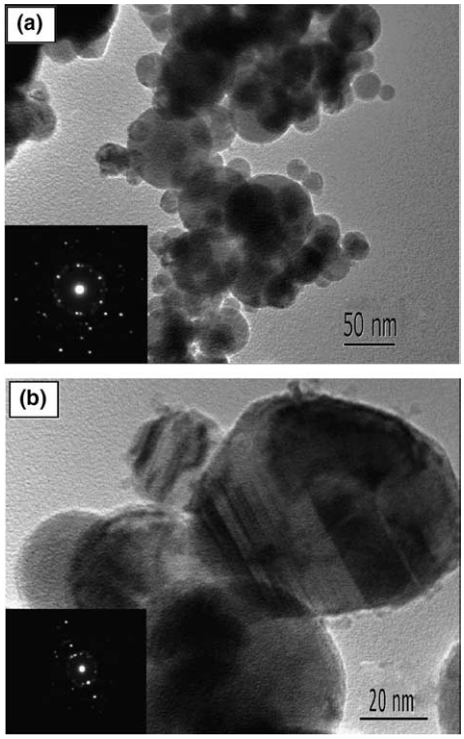

Fig. 1. TEM images of nano-size TiNi powders (inset diffraction pattern in (a) shows austenite structure, while that in (b) shows martensite structure).