Intermetallics 83 (2017) 43–54

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Investigating the influence of Ti powder purity on phase evolution during NiTi sintering using in-situ neutron diffraction

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ARTICLE INFO

Article history:
Received 30 March 2016
Received in revised form
29 November 2016
Accepted 1 December 2016

Keywords:
Shape-memory alloys
In-situ
Phase transformation
Reaction synthesis
Differential scanning calorimetry
Diffraction/scattering

ABSTRACT

The influence of Ti powder purity on phase evolution during the reactive sintering of elemental Ni and Ti powders to form NiTi was studied using differential scanning calorimetry (DSC) and in-situ neutron diffraction. Reaction between the Ni and Ti is not significant until 600 °C. From 600 to 700 °C, Ti_2Ni forms in mixtures made from high (HP) and low purity (LP) Ti powder. The Ni_3Ti phase also grows in this temperature range in the LP mixture. The most significant phase evolution takes place between 700 and 920 °C. The α to β phase transformation in (Ti) begins at the eutectoid temperature (765 °C) and ends at 820 °C. The highest growth rates for all three intermetallic phases, including NiTi, and the decay rate of the elemental Ni occur in this temperature range. At approximately 1000 °C, all reactants are consumed and homogenization occurs, with NiTi continuing to grow at the expense of the other intermetallic phases. The Ti rich intermetallic phase persists above its melting point, due to the formation of a solid-solution with oxygen (i.e. $Ti_2Ni(O)$). From 1100 to 1200 °C, the microstructure becomes a stable mixture of NiTi with a small fraction of $Ti_2Ni(O)$. The phase evolution is similar in the LP and HP mixtures. However, the rate of reaction is higher in the LP mixture due to the influence of impurities (O, Fe and Ni) on the diffusivities in the many phases involved.

1. Introduction

NiTi is a shape memory alloy used across many industries from aerospace to dental/medical applications due to its strength, large recoverable deformations, good wear resistance and biocompatibility. Typical wrought production routes involve vacuum induction melting (VIM) and vacuum arc re-melting (VAR) of the base materials. These are expensive processes which are limited to the production of relatively simple geometries. Expensive machining operations are then required to produce more complex components. Powder metallurgy may offer an alternative cost-effective route to produce high quality near-net shape components. Research on the production of NiTi components via powder metallurgy methods has focused on the use of pre-alloyed powders to ensure high purity, compositional and microstructural homogeneity, and good density [1–9]. Reactive sintering using elemental powders has also been investigated to avoid the costs and difficulties associated with producing alloy powders [10–26]. The main problems plaguing the reactive sintering method have been purity (O_2 contamination, especially in the Ti powders), poor homogeneity in the final part, and difficulty in achieving high density.

To deal with these issues, previous investigations have looked at alternative sintering techniques including Hot Isostatic Pressing [4,27–29] and the use of calcium reductant vapour [15]. Research has also been performed on the effects of powder size [19,21,30]. Recently, Cluff and Corbin [30] have shown that Ti powder purity can play a more important role in the reactive sintering of NiTi than Ti powder size. Their results from differential scanning calorimetry (DSC) indicated a larger difference in intermetallic formation between low purity powder and high purity powder of approximately the same size than between two high purity powders whose size was a factor of three different.

However, until the past few years, work reported in the literature centered on post sintering analysis or interrupted sintering for an understanding of the reaction sequence. Recently, Chen, Liss and Cao [24,25] performed in-situ neutron diffraction (ND) experiments to study the reactive sintering of Ni-rich NiTi (49 at% Ti: 51 at% Ni) using Ti and TiH_2 powders. In both publications, the Ni/TiH_2 powder mixture showed delayed intermetallic formation compared to the elemental Ni/Ti powder mixture during heating.

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http://dx.doi.org/10.1016/j.intermet.2016.12.001

However, the Ni/TiH_2 mixture resulted in more NiTi after cooling. This was largely attributed to a eutectoid decomposition of NiTi → Ni_3Ti + Ti_2Ni observed during cooling. These authors have also used in-situ ND to investigate the sintering behaviour of NiTi from elemental Ni and Ti (49 at% Ti: 51 at% Ni) during holds at 880, 950 and 1100 °C [26] using a similar purity of Ti as the high purity powder used by Cluff and Corbin [30]. Their results indicated that as the elemental Ni and Ti disappeared, the phase fraction of intermetallic phases grew (Ti_2Ni, NiTi, Ni_4Ti_3, Ni_3Ti). The continued growth of NiTi was a result of the decomposition of the other intermetallic phases present. The Ti_2Ni phase is present at temperatures above the peritectic (984 °C) where it is expected to be a liquid. The reason for the continued existence of the phase beyond this temperature is given in one publication [26] as an oxide shell around the phase. Again the decomposition NiTi → Ni_3Ti + Ti_2Ni during cooling was observed. Their analyses on phase evolution is incomplete as Ti is considered a single phase throughout the whole temperature range despite the allotropic phase transformation α-Ti → β-Ti that will have an impact on phase evolution. Another study on NiTi using in-situ neutron diffraction performed by Cluff, Gharghouri and Corbin [31] investigated the role of powder size in the reactive sintering of NiTi. They reported slower intermetallic formation rates in the coarser Ni powders compared to coarser Ti powders. The continued presence of the Ti_2Ni phase above its expected melting temperature was also noted. It was suggested that O was responsible for stabilizing the phase but further work was required to fully understand what was occurring. In all of the above in-situ neutron diffraction investigations, the effect of Ti powder purity on phase evolution was not considered.

The present investigation aims to further understand the influence of titanium powder purity on phase evolution during reactive sintering from elemental powders to produce NiTi. Differential scanning calorimetry (DSC) and in-situ neutron diffraction (ND) have been employed to determine the temperature ranges over which the various reactions take place, as well as the relative quantity and nature of the phases present during sintering.

2. Materials and methods

One Ni powder and two Ti powders were used. The Ni powder was Vale Inco carbonyl powder type 123 (Inco 123 Ni). Both Ti powders were hydride-dehydride (HDH) −325 mesh powders obtained from Alfa Aesar. The first had a purity of 99.5 wt% Ti (metals basis) and the second a purity of 99.99 wt% Ti (metals basis), referred to henceforth as LP Ti and HP Ti, respectively. Both −325 mesh Ti powders were sieved to −400 + 500 (25–38 μm) mesh to ensure consistency between the two powders.

The three elemental powders were carefully characterized prior to the DSC and ND experiments. Powder morphology was studied using a Hitachi S-4700 FE-SEM, powder size was determined using a Malvern Master Particle Sizer model 2600c, and apparent density was measured using an Arnold meter. Hydrogen (on a LECO RH-404), carbon (on a LECO CS-444), oxygen (on a LECO TC-436), and nitrogen (on a LECO TC-436) analyses were performed at ATI Wah Chang (Albany, Or). Inductively coupled plasma optical emission spectroscopy (ICP_OES) analyses were carried out at the Minerals Engineering Center (Dalhousie University, Halifax, NS) to determine the metallic contaminants.

SEM micrographs of the starting Ti powders are shown in Fig. 1. The morphologies of the LP and HP Ti powders are very similar, showing flat faced angular particles typical of an HDH Ti powder. Table 1 lists the D_{50} of the sieved elemental powders. The D_{50} of the HP Ti is larger than that of the LP Ti (36 μm vs. 28.5 μm). The powder size distributions are shown in Fig. 2. Apparent density values for the sieved elemental powders are also given in Table 1, along with % relative (or % theoretical) density based on theoretical densities of 8.9 and 4.51 g/ml for Ni and Ti, respectively. The HP Ti has a higher apparent density than the LP Ti, which is thought to be due to the differences in powder size.

The results of the chemical analysis on the elemental powders are listed in Table 2. The HP Ti has a lower oxygen content than the LP Ti, as expected. The hydrogen content of both powders is higher than the acceptable limit for any of the ASM designations for commercially pure (CP) Ti (grades 1 to 4). The excess hydrogen is likely due to the powders not being fully de-hydrided. Discounting the hydrogen, the HP Ti is grade 3 while the LP Ti does not fit into any designation. Table 2 shows that the LP Ti has 6.5 times more Fe and 3.5 times more Ni than the HP Ti. For the other metallic elements, this ratio falls between 1.5 and 2.

Following characterization, the elemental powders were mixed to a composition of 51 at% Ti - 49 at% Ni, resulting in 2 different powder mixtures: an LP Ti - Inco 123 Ni mixture (*LP mixture*) and an HP Ti - Inco 123 Ni mixture (*HP mixture*). The mixtures were subsequently dry milled for 2 h in a glass jar. The apparent densities of the mixtures were measured and their compaction properties were determined by uniaxially compacting 0.79 ml of powder in a 12.5 mm diameter die at 200, 400, 600 and 850 MPa. To calculate density, the specimens were weighed, and their dimensions measured using a micrometer. The apparent densities and the compaction curves for the two mixtures are reported elsewhere [30]. The HP mixture has a marginally higher apparent density than the LP mixture. The compaction curve of both mixtures overlapped indicating little difference in density between the two mixtures for a given pressure throughout the range of compaction pressure.

The green microstructures of the two mixtures pressed at 860 MPa are presented in Fig. 3. The dark gray phase is Ti and the light gray phase is Ni. The Ti, Ni, and pore distributions, morphologies, and dimensions are similar in the two mixtures, indicating

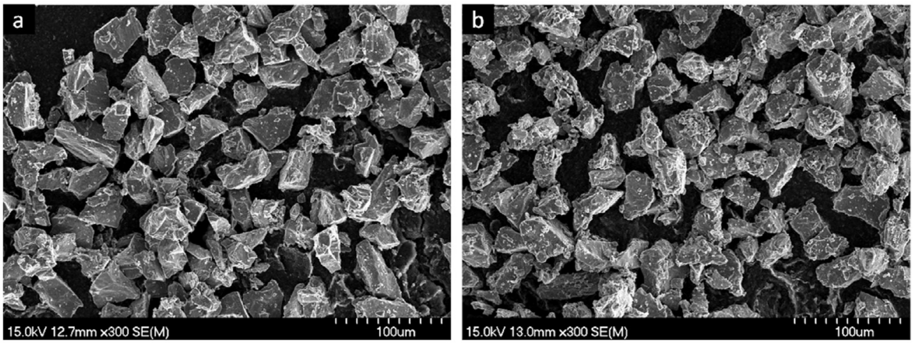

Fig. 1. SEM micrographs of sieved elemental Ti powders a) LP Ti and b) HP Ti.