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In situ observation and neutron diffraction of NiTi powder sintering

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Abstract

This study investigated NiTi powder sintering behaviour from elemental powder mixtures of Ni/Ti and Ni/TiH_2 using in situ neutron diffraction and in situ scanning electron microscopy. The sintered porous alloys have open porosities ranging from 2.7% to 36.0%. In comparison to the Ni/Ti compact, dehydrogenation occurring in the Ni/TiH_2 compact leads to less densification yet higher chemical homogenization only after high-temperature sintering. For the first time, direct evidence of the eutectoid phase transformation of NiTi at 620 °C is reported by in situ neutron diffraction. A comparative study of cyclic stress–strain behaviours of the porous NiTi alloys made from Ni/Ti and Ni/TiH_2 compacts indicate that the samples sintered from the Ni/TiH_2 compact exhibited a much higher porosity, larger pore size, lower fracture strength, lower close-to-overall porosity ratio and lower Young's modulus. Instead of enhanced densification by the use of TiH_2 as reported in the literature, this study shows an adverse effect of TiH_2 on powder densification in NiTi.

Keywords: Shape memory alloys; Porous material; Reactive sintering; Mechanical behaviour; Hydrogen desorption

1. Introduction

Equiatomic NiTi possesses a combination of a unique shape memory effect and pseudoelastic properties with high strength, large energy absorption, good corrosion resistance and excellent biocompatibility, and has therefore been used in a wide range of applications such as mechanical couplings, actuators and medical devices [1]. A few comprehensive reviews have reported on the fabrication methods used to produce NiTi [2–4]. Porous NiTi alloys have been receiving increasing interest in biomedical applications because a porous structure not only further decreases the Young's modulus of the material but also promotes bone tissue ingrowth. Among the manufacturing techniques for cellular NiTi alloys, a conventional press-and-sinter process is a widely used, simple and cost-effective technique [4]. In terms of starting powder selection when the press-and-sinter method is introduced, blended elemental (BE) powders are generally preferred to pre-alloyed (PA) powders. This is because BE powders are not only much more affordable but also exhibit much better compressibility as compared with PA powders.

Recently, enhanced densification using TiH_2 as a replacement of Ti powder has been realized in Ti and its alloys by powder metallurgy (PM) [5,6]. The possible reasons for the enhanced densification observed in Ti alloys when TiH_2 is used were summarized by Wang et al. [7]. First, TiH_2 powder has better compressibility due to reduced cold welding between TiH_2 particles and significant powder fragmentation during compaction [8], thus achieving a high green density. Second, TiH_2 helps reduce the oxygen content in sintered Ti because dehydrogenation provides a reducing sintering atmosphere [9]. Third, TiH_2 has better sinterability: >99% sintered density is readily achievable. This may be the result of the defects formed during the dehydrogenation process, which accelerates mass transport for densification [8]. Because of these

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attributes, many Ti alloys have been explored using TiH_2 powder, including pure Ti, Ti–6Al–4V, Ti–5Al–2.5Fe and TiAl [6,8,10–13]. In the case of PM NiTi, the use of TiH_2 also seems to result in a higher degree of sintering, reduced pore size and a more uniform pore size distribution [14–18]. However, this enhanced densification is debatable and the sintering mechanism when TiH_2 is involved is not well understood. Recently, Robertson and Schaffer [19] observed a discouraging densification and a much larger porosity when TiH_2 powder is used. This is consistent with our recent study [20]. However, they believed the resultant higher porosity was not due to hydrogen release, but rather to the evaporation of contaminant in the TiH_2 powder. It should be pointed out that the particle size of TiH_2 used in many reports (e.g. [14–16]) is much smaller than that of Ti. Therefore, Ni/TiH_2 compact usually has a higher green density than Ni/Ti compact, and thus it is not surprising to observe a higher sintered density in Ni/TiH_2 compact. Hence, it is not clear whether the observed higher densification is caused by the dehydrogenation of TiH_2 or is simply due to the higher green density resulting from the smaller particle size in TiH_2 compact. As a matter of fact, in the production of porous NiTi alloys TiH_2 powder is normally used as a foaming agent, as it also is in aluminum metallic foams. Thus, it is of great importance to clarify whether or not the use of TiH_2 benefits densification in PM NiTi alloys, and in particular whether or not the dehydrogenation enhances sintering.

Apart from the densification, another equally important aspect in PM NiTi is how to achieve a single B2 phase. Even though PM techniques have successfully produced NiTi alloys, these products are never single phase. The as-sintered NiTi alloys always contain other phases, e.g. $NiTi_2$, Ni_3Ti or Ni_4Ti_3. Some reports attribute this to the incomplete reaction between Ni and Ti powders [21] or the eutectoid phase transformation occurring at 630 °C [22–25]. However, many others do not believe in the existence of such eutectoid decomposition [26–32]. Clarification of this eutectoid transformation has been a long-sought challenge over the past six decades [32]. In 1950, Duwez and Taylor [22] first reported the decomposition of NiTi into Ni_3Ti and $NiTi_2$ at 800 and 650 °C. However, a subsequent study in 1953 by Margolin et al. [26] refuted the existence of such a eutectoid reaction in a high-purity NiTi. This problem was also investigated by Koskimaki et al. [24], who found that NiTi eutectoidally decomposes into Ni_3Ti, $NiTi_2$ and an intermediate phase ("X-phase" in their paper) upon prolonged aging for 1 month at 600 °C. In contrast, Nishida et al.'s report [31] revealed no such secondary phases present in a 50Ni–50Ti alloy upon furnace cooling and water quenching from 1000 °C. In the same report [31], Nishida et al. also investigated the precipitation sequence of intermetallics during ageing of a Ni-rich 52Ni–48Ti alloy, which they reported as $NiTi \rightarrow Ni_4Ti_3 \rightarrow Ni_3Ti_2 \rightarrow Ni_3Ti$ with Ni_3Ti being the equilibrium phase; they claimed no eutectoid reaction existed in their system. The debate of whether or not the eutectoid reaction exists has recently been reviewed by Otsuka and Ren [32]. They suggest that this eutectoid phase transformation seems unrealistic, given the lack of direct evidence [37]. Nevertheless, we should note that all of these studies utilized ex situ laboratory X-ray diffraction (XRD), which suffers from insufficient penetration into metallic samples and lack of intensity. These technical limitations can be overcome with high-energy synchrotron X-ray and neutron diffraction, now available at reactors and spallation sources [33,34]. Synchrotron and neutron radiation is able to penetrate bulk metals and this type of diffraction has been successfully employed for in situ studies of metal sintering and phase transformations [35]. The beam intensities allow information from bulk material to be followed on short time scales, while undergoing an in situ heating/cooling cycle to observe phase transformations.

To the best of our knowledge, a comparative study using Ti and TiH_2 powders to fabricate NiTi alloys has not been reported; more specifically the influence of hydrogen release from TiH_2 powder on densification and chemical homogenization, and first-hand evidence of eutectoid decomposition are lacking. This work is an companion to our recently published report [36]. In the present study, in situ neutron diffraction was applied, for the first time, to the quantitative investigation of NiTi powder sintering and to the phase evolution upon in situ heating and cooling. Ex situ laboratory XRD was also performed alongside the neutron diffraction. In addition, we also used an environmental scanning electron microscopy technique to observe in situ microstructural evolution during dehydrogenation of TiH_2. In brief, the purpose of this study is (i) to investigate the microstructure, phase transformation and mechanical properties of NiTi alloys prepared from powders of Ni with either elemental Ti or TiH_2; (ii) to investigate the effect of hydrogen release during sintering on densification, chemical homogenization and mechanical properties; (iii) to present direct proof to clarify whether or not the eutectoid reaction happens during furnace cooling, by conducting in situ neutron diffraction; and (iv) to discuss the sintering mechanism involved in TiH_2 powder.

2. Experimental

2.1. Materials

The mean particle sizes of the starting Ti, TiH_2 and Ni powders were 32.2, 24.6 and 16.4 μm, respectively. Two batches of powder mixture, i.e. Ni/Ti and Ni/TiH_2, both having a nominal composition of 51 at.% Ni and 49 at.% Ti, were gently mixed in a ball mill for 10 h. No binder or lubricant was added during mixing.

2.2. Pressing and sintering

After mixing, the powder mixture was compacted in a single-action steel die under 250 MPa pressure. Stearic acid as a lubricant was lightly applied to the die wall before