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Shape-memory NiTi with two-dimensional networks of micro-channels

Anselm J. Neurohr, David C. Dunand *

Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

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ABSTRACT

A process was developed for fabricating arrays of micro-channels in shape-memory NiTi for bone implant applications, with a tailorable internal architecture expected to improve biomechanical compatibility and osseointegration. Ni–51.4 at.% Ti with 24–34 vol.% porosity was fabricated by electrochemical dissolution of parallel layers of steel wire meshes embedded within a NiTi matrix during hot pressing of NiTi powders. The resulting NiTi structures exhibit parallel layers of orthogonally interconnected micro-channels with 350–400 μm diameters that exactly replicate the steel meshes. When low-carbon steel wires are used, iron diffuses into the surrounding NiTi during the densification step, creating a Fe-enriched zone near the wires. For high-carbon steel wires, TiC forms at the steel/NiTi interface and inhibits iron diffusion but also depletes some titanium from the adjacent NiTi. In both cases, the NiTi regions near the micro-channels exhibit altered phase transformation characteristics. These NiTi structures with replicated networks of micro-channels have excellent potential as bone implants and scaffolds given: (i) the versatility in channel size, shape, fraction and spatial arrangement; (ii) their low stiffness (15–26 GPa), close to 12–17 GPa for cortical bone; (iii) their high compressive strength (420–600 MPa at 8–9% strain); and (iv) their excellent compressive strain recovery (91–94% of an applied strain of 6%) by a combination of elasticity, superelasticity and the shape-memory effect.

1. Introduction

Porous metals for implant applications – represented mainly by tantalum, stainless steel, chromium–cobalt, titanium, and nickel titanium (NiTi) [1–3] – have two main advantages over their monolithic counterparts. First, open pores, when ranging from 100 to 600 μm in size, permit bone ingrowth, which improves the long-term fixation of the implant at the bone/implant interface [4,5]. Second, porosity lowers the implant stiffness and thus reduces stress-shielding originating from the large stiffness mismatch existing between bone and implant. Stress-shielding leads to implant failure by causing bone resorption and implant loosening [2]. Of the above bulk metallic implant materials for load-bearing implant applications, NiTi has the lowest Young's modulus (68 GPa [6]) and is thus particularly suitable for reducing stress-shielding. Porous NiTi has previously been fabricated [7,8] with average stiffness values as low as that of cortical bone (12–17 GPa) or even cancellous bone (<3 GPa) [9].

During the initial linear range of the stress–strain curve, NiTi can exhibit an apparent stiffness well below its already low Young's modulus as a result of reorientation of existing twins (for shape-memory martensitic NiTi) or creation of stress-induced twins (for superelastic austenitic NiTi). Further large-scale twin-mediated deformation can accrue in the stress plateau of NiTi, beyond the macroscopic yield point, with compressive strains of ~4% (well beyond the elastic limit of bone, ~1–2% [9,10]) that can be recovered completely upon heating (for shape-memory NiTi) or removal of the stress (for superelastic NiTi) [11]. Also, superelasticity delays the onset of plasticity at stress concentrators such as pores [12] and increases the material's energy absorption and damping capacity [13,14]. Finally, the superelastic and shape-memory effects can provide a mechanism for deploying and fixating the implant, similar to NiTi stents and staples [15].

To permit bone ingrowth while retaining low stiffness, high strength, and high superelasticity/shape-memory in porous NiTi, it is important to control the pore size, shape, volume fraction, and connectivity during processing. Fabrication of NiTi foams has to date been performed almost exclusively by the powder metallurgy route, using either elemental or pre-alloyed powders, as reviewed in Ref. [4]. Powder metallurgy techniques used for creating porous NiTi include partial powder sintering [16–25], transient liquid phase sintering [26,27], expansion of argon entrapped during hot isostatic pressing (HIP) of powders [28–31], self-propagating high-temperature synthesis (SHS) [7,32–38], metal injection molding (MIM) followed by sintering or SHS [39,40], and combinations of these techniques with various space-holder materials. Also, laser engineered net shaping (LENS) [41] and selective laser sintering (SLS) [42,43] have recently been employed to fabricate NiTi scaffolds from powders.

* Corresponding author. Tel.: +1 847 491 5370.
E-mail address: dunand@northwestern.edu (D.C. Dunand).

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Partial powder sintering produces pores whose size and shape are constrained by the initial powder size. Pore sizes are smaller than the powders and foam strength is often compromised due to the irregular pore shape [16]. Expansion of entrapped argon gas also produces only low porosities due to the high creep strength and low creep ductility of NiTi [29,31]. SHS from elemental powders produces inhomogeneous porosity and allows only limited control over pore characteristics. Furthermore, it often forms intermetallic phases such as Ti_2Ni, Ni_3Ti, and Ni_4Ti_3 that lack the superelastic properties of NiTi and can embrittle the NiTi phase [7,16,37]. LENS and SLS are capable of tailoring pore characteristics closely but often fail to achieve full powder densification, resulting in a significant amount of closed porosity [41–43].

Sintering metallic powders in the presence of a space-holder creates pores whose size, volume fraction and morphology are controlled independently and easily by the space-holder. Temporary space-holders used for NiTi include ammonium bicarbonate [44–46], polymethyl methacrylate [40] and magnesium [47]. Removal of these space-holders occurs by thermal decomposition or evaporation and can thus be integrated into the sintering processing stage. On the other hand, permanent space-holders such as sodium chloride [8,40,48] and sodium fluoride [49] are removed subsequent to high-temperature densification of the NiTi matrix. While permanent space-holders thus require an additional processing step, they prevent pore collapse when powder densification occurs under an externally applied pressure (unlike temporary space-holders that are removed early in the sintering process), thereby allowing more complete NiTi powder densification, e.g., by HIP or hot die pressing.

All previous accounts of NiTi foams created by the space-holder method describe materials with equiaxed pores. However, interconnected elongated pores or micro-channels would more closely mimic the internal pore architecture of bone and could be used to tailor the implant mechanical properties (in particular, stiffness, strength and ductility) by controlling their orientation [50]. Moreover, micro-channels provide unobstructed access for the penetration of bone deep into the implant, unlike fenestrations between rounded pores that can restrict access from one pore to another, as discussed in Ref. [8]. Recent work by Dunand and co-workers [51–53] demonstrated a novel technique for creating metallic foams with elongated, interconnected micro-channels: low-carbon steel wires woven into meshes were used as permanent space-holders in commercially pure titanium and alloyed Ti–6Al–4V and were removed electrochemically after the powder densification step. Iron diffused a few tens of micrometers around the wires into the titanium matrix, and this Fe-rich zone could be removed along with the space-holder to increase the final micro-channel diameter. Conversely, if the steel was first carburized, titanium carbide (TiC) formed at the steel/titanium interface inhibiting Fe diffusion, so that the micro-channels exactly replicated the wire diameter.

In this work, we demonstrate the use of steel wire meshes as space-holders for the fabrication of porous shape-memory NiTi. This technique, which to date has been used only for Ti and Ti–6Al–4V [51–53], permits an unprecedented degree of control over the final pore characteristics in NiTi, enabling for the first time the fabrication of porous NiTi with elongated, aligned, and orthogonally interconnected micro-channels and a fully densified matrix. These porous structures possess a microstructure, phase transformation, and mechanical behavior suitable for load-bearing bone implants.

2. Experimental procedures

2.1. Materials

To avoid compositional fluctuations from the use of elemental powders, pre-alloyed NiTi powders (from Special Metals Corp., NY) with a nominal composition of 48.6 at.% Ni and 99.9% purity were used as in previous research [8,27,49]. The powders, which were sieved to a size range of 63–177 μm, are nearly spherical in shape and have a smooth surface and small satellites (Fig. 1a), suggestive of fabrication by liquid spraying.

The space-holders were low-carbon steel wire meshes woven in an orthogonal pattern. Two types of meshes (supplied by McMaster-Carr, Elmhurst, IL) were used, resulting in different final porosities: the first consisted of 356 μm diameter wires spaced 711 μm apart with an open area of 44% (referred to hereafter as "coarse meshes", Fig. 1b); and the second had 406 μm diameter wires spaced 432 μm apart with an open area of 27% (referred to as "fine meshes", Fig. 1c). The meshes were embedded in pure carbon powders within steel envelopes and pack-carburized at 960 °C for 2 h. The goal of this operation was to supply enough carbon to the wire so that a TiC surface layer could form at the steel/NiTi interface during hot-pressing to prevent interdiffusion between the two phases, as shown previously for Ti and Ti–6Al–4V [51–53].

2.2. Composite densification

Three composites were made by pouring layers of NiTi powders alternating with meshes (cut into disks with 25 mm diameter) into a 25.4 mm diameter die, resulting in ~14 mm tall cylindrical steel/NiTi composites after powder densification. Prior to pressing, the TZM die and pistons were coated with boron nitride to reduce friction. Parallelism of the meshes was ensured by manually compacting and leveling each individual layer of NiTi powders.

For the first NiTi/steel composite, five layers of 3 g of NiTi powders were poured, alternating with four coarse steel meshes. Each mesh has been carburized for a different time: 0, 2, 5, and 9 h. This composite, and the porous specimens created from it, are labeled hereafter as C for "carburization" (since it was used to determine the effect of carbon content).

A second composite was created by pouring 19 layers of 1.74 g of NiTi powders alternating with 18 fine steel meshes previously carburized for 2 h. To achieve in-plane isotropy, the orientation of the meshes was varied in the following order: 0°, −15°, +15°, −30°, +30°, −45°, −38°, +38°, −23°, +23°, −8°, +8°, 0°, −15°, +15°, −30°, +30°, −45°, 0°. This composite and specimens cut from it are labeled HP (for "high porosity"). Likewise for the third composite (called LP, for "low porosity"), 18 layers of 2.1 g of NiTi powders were poured into the die, alternating with 17 coarse meshes oriented in the same isotropic manner. The amounts of NiTi powders between each mesh for the LP and HP composites were chosen such that the distance between the meshes after powder densification was the same (~50 μm) for both samples. Thus, the final porosities are predicated solely on the wire area density of the two types of meshes used, not on the thickness of dense NiTi between the meshes. Lastly, a monolithic NiTi control sample was made by the same method without steel meshes.

The mesh/powder preforms were densified by hot-pressing at 1020 °C (below the >1100 °C eutectic point in the Fe–Ni–Ti ternary system [54]). For specimen HP, a uniaxial pressure of 40 MPa was applied for 3 h, followed by an additional 3 h at 60 MPa to complete densification. For specimens LP and C and for the monolithic control sample, a pressure of 60 MPa was applied for 3 h. The hot press, which is described in more detail elsewhere [55], was evacuated to 10^{-6} torr residual pressure. Densification was monitored continuously using a displacement transducer and deemed complete when the piston displacement became negligible. The densified composites were then cooled at very low stress (~0.5 MPa) to room temperature in vacuum over ~3 h.

Several 5 × 5 × 10 mm parallelepipeds were cut from the hot-pressed composites by electric discharge machining (EDM), exposing the steel wires to their surfaces and with their long sides