Porous NiTi with Superelastic or Shape-Memory Properties

Ampika Bansiddhi and David C. Dunand Northwestern University Evanston, Illinois

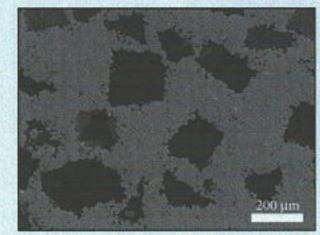
porosity (90% open-pore ratio) and 100 to 400 micron pore size has been fabricated by a new foam replication process. Prealloyed NiTi powders are densified in the presence of NaCl powders by hot isostatic pressing at temperatures above the melting point of the NaCl space holder (800°C, 1470°F). The NaCl space holder can be fully removed by water dissolution or vacuum evaporation without unacceptable residual or contamination. Empty space left after removal of NaCl becomes pores whose fraction, size, shape, and connectivity are controllable through the initial volume fraction and geometry of the NaCl space holders.

The pores maintained the angular shape of the original NaCl particles, indicating that substantial NiTi densification occurred prior to NaCl melting (Fig. 1). With this technique, higher porosity and connectivity can be achieved by the choice of space-holder content and geometries, while thinner NiTi walls are well-densified without pore collapse, which is problematic in a simple sintering approach with transient space holders. Subsequent sintering after NaCl removal at temperatures above the limits of the HIP process can also further optimize densification in the NiTi structure.

Molten space holders offer significantly greater flexibility in processing, relative to other existing solid place holders (fluorides or oxides), by enabling cheaper and more low-melting space-holders with high solubility in water. For example, NaCl could be used for foams of technologically-important high-melting-point materials, including the NiTi alloy studied here. Furthermore, for porous NiTi to serve as a bone-replacement implant, this method offers precise control over many foam geometrical parameters that are crucial to the performance of the implant.

The NiTi foams exhibit superelasticity or shapememory properties, depending on the exact Ni/Ti ratio. Higher nickel content could be applied directly to the technique (although the method was originally demonstrated using porous shape-memory NiTi) to create low-modulus, superelastic NiTi foam.

In general, high compressive yield strength with very low stiffness (<20 GPa) and large recovery strain (>4%) are observed. For example, martensitic



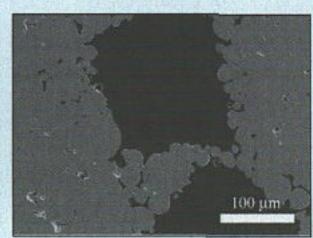


Fig. 1 — Scanning electron microscopic micrographs of NiTi foam polished cross-sections showing open porous structure at low magnification (left) and high magnification (right).

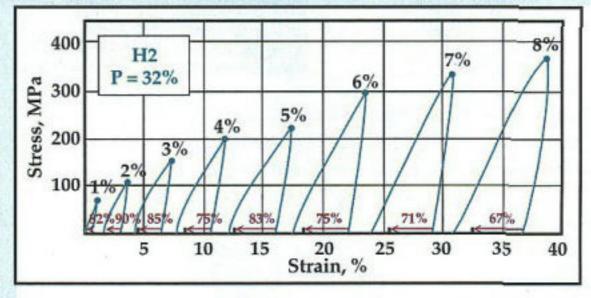


Fig. 2 —
Typical loadunload-heat
recovery cycling
of porous NiTi
from 1-8%
applied strain.
Curves are
shifted along
X-axis.

porous NiTi densified by HIP at 1065oC (1950°F) for four hours shows a compressive stress as high as 1855 MPa at a plastic compressive strain of 55%. Figure 2 shows the stress-strain curve of porous NiTi, which can be characterized by:

- a near linear loading branch, with an average stiffness of 4 to 6 GPa due to a combination of elastic and detwinning deformations;
- a near-linear unloading branch, with a higher stiffness of 10 to 25 GPa due to elastic recovery strains;
- a shape-memory recovery strain and unloading strain increasing linearly with the maximum applied strain, and reaching a value of ~4% and 2%, respectively, for an applied strain of 8%.

In conclusion, NiTi foams produced by the molten NaCl space-holder method are excellent candidates for bone implant applications, because they exhibit a unique combination of attributes:

- Simple processing route,
- Desirable mechanical properties (low effective stiffness to alleviate stress shielding; high strength and ductility to prevent failure; shape-memory capability useful to operative deployment of the foam),
- Biocompatibility for NiTi and very low toxicity for NaCl (if traces remain in the foam); and
- Large pores fully open to the surface (for bone ingrowth).

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For more information: David C. Dunand, Northwestern University, Evanston, IL 60208; tel: 847/491-5370; dunand @northwestern.edu; www.northwestern.edu.