JMEPEG (2011) 20:511–516
DOI: 10.1007/s11665-010-9827-6

1059-9495/$19.00

Processing of NiTi Foams by Transient Liquid Phase Sintering

Ampika Bansiddhi and David C. Dunand

(Submitted May 24, 2010)

Porous NiTi was produced by sintering pre-alloyed NiTi powders (with small Ni addition to form Ni-rich composition) with NaCl powders which are removed to create 40-60 vol.% macropores which are open to the surface, blocky in shape, and 100-400 µm in size. The microporosity present between the NiTi powders is infiltrated by an in situ created NiTi-Nb eutectic liquid which, after solidification, densifies the NiTi powders into dense struts. This processing technique allows for separate control of the macroporous structure, and the densification and composition of the NiTi struts.

Keywords bone implant, eutectic, microstructure, porous, shape memory

1. Introduction

Porous NiTi is attractive for biomedical applications because of the biocompatibility, high compressive strength, and shape recovery (from either the shape memory or superelastic mechanism) of NiTi, and the reduction in stiffness and increase osseo-integration offered by the pores (Ref 1). Several methods use space-holder materials to achieve good control over pore size, shape, and volume fraction (Ref 2-5). However, many of these methods result in poor densification of the NiTi powders into walls or struts (for brevity, we use in the following only the word "strut") due to the low sintering ability of NiTi and the presence of the space-holders. Insufficient densification within the NiTi struts of these foams, which may lead to poor fatigue resistance, can be addressed by hot isostatic pressing (HIP) of pre-alloyed NiTi powders mixed with NaCl space-holder (Ref 6). HIP processing, however, adds to the cost of the foam, and so a method relying on sintering is desirable.

Recently, we demonstrated an approach that uses a transient liquid to promote densification of the NiTi powders (Ref 7). A eutectic liquid, created by reaction between pre-alloyed Ti-rich NiTi powders and niobium powders, fills the space between the NiTi particles of the foam matrix without filling the macropores previously created by NaCl space-holders. Bansiddhi and Dunand (Ref 7) showed that transient liquid phase sintering can be performed on NiTi structures containing a high fraction (40%) of large pores, and that it produces desirable mechanical properties (high compressive strength and low stiffness) at relatively low processing temperatures (1185 °C). Moreover, the resulting porous NiTi-Nb material, which is biocompatible (Ref 8), exhibits the same shape memory effect as porous NiTi (Ref 7).

The goal of this study is to adapt the above liquid phase sintering method from Ti-rich, shape-memory NiTi (Ref 7) to Ni-rich, superelastic NiTi. Pre-alloyed NiTi powders are again used to avoid the non-uniform composition and contamination often observed in NiTi foams produced from elemental Ni and Ti powders (Ref 1). Small additions of Ni powders are added to the pre-alloyed NiTi powders to create the Ni-rich composition needed for superelastic properties, and Nb powders are furthermore added to generate a transient liquid phase which fills the space between the NiTi powders within the struts.

2. Experimental Procedures

Four types of powders were used: pre-alloyed NiTi (48.6 at.% Ni, Special Metals Corp., NY) sieved to 44-63 µm, Ni (99.9% purity, 3-7 µm, Alfa Aesar, MA), Nb (99.8% purity, 1-5 µm, Alfa Aesar, MA), and NaCl (99% purity, Alfa Aesar, MA) sieved to 100-250 µm. Two preparation routes were used to make powder compacts: (1) homogeneous powder mixing; and (2) powder layering.

The first route mentioned above consists of three mixing steps, all performed in a twin-shell dry blender: (i) pre-alloyed NiTi are mixed with 2.2 at.% Ni and blended for 2 h to create a Ni-rich NiTi mixture (50.8 at.% Ni and 49.2 at.% Ti); (ii) this Ni-rich NiTi blend is mixed with 3.1 at.% Nb (94.7 wt.% NiTi and 5.3 wt.% Nb) and blended for an additional 2 h; and (iii) the NiTi-Nb mixture is mixed with 40 vol.% NaCl space-holder powders and blended for 2 h. The resulting homogeneous NiTi/Ni/Nb/NaCl blend was cold pressed at a pressure of 350 MPa into a green preform with 10-mm height and 12.7-mm diameter. The preform was sintered at 1185 °C for 10 h (heating rate: 7 °C/min) in a high-vacuum furnace with titanium getters, resulting in a porous sample labeled 1.

This article is an invited paper selected from presentations at Shape Memory and Superelastic Technologies 2010, held May 16-20, 2010, in Pacific Grove, California, and has been expanded from the original presentation.

Ampika Bansiddhi, Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand; and **David C. Dunand**, Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208. Contact e-mail: dunand@northwestern.edu.

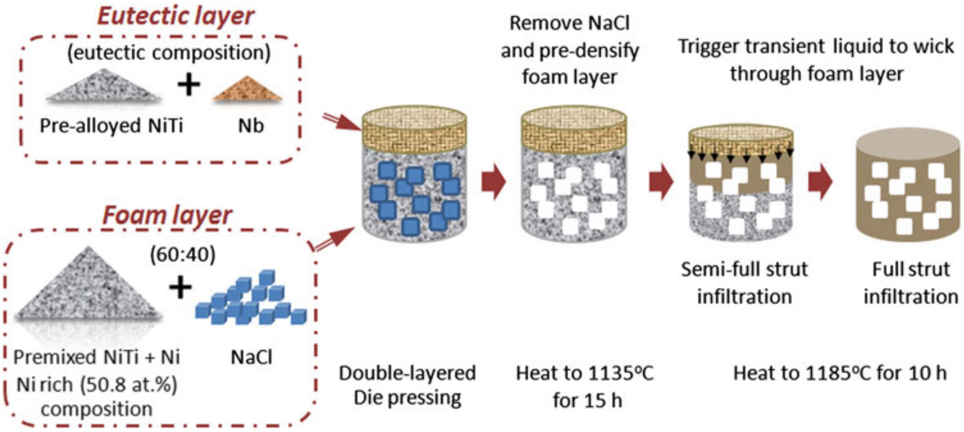

Fig. 1 Schematic of the double-layer method

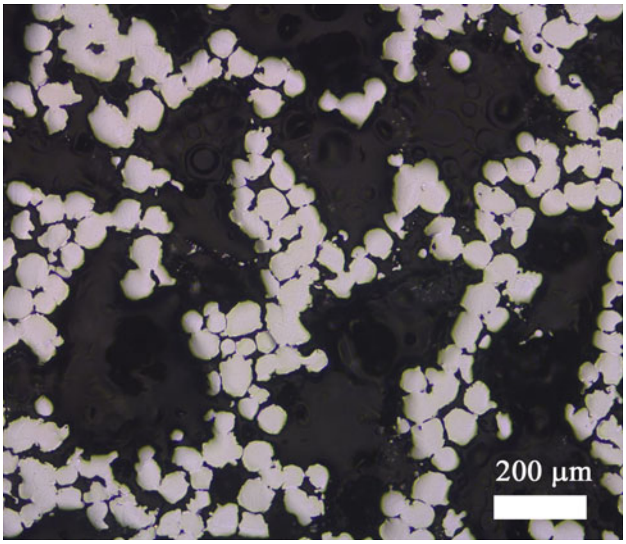

Fig. 2 Optical micrograph of a cross section from the as-sintered foam 1, made using a single NiTi/Ni/Nb/NaCl layer; pores are black, metal is light

The second route (Fig. 1) creates a preform with two chemically distinct layers: a Ni-rich NiTi blend for the lower layer, and a NiTi-Nb eutectic mixture for the upper layer. The lower layer is made as previously by mixing near-equiatomic (48.6 at.% Ni) NiTi with 2.2 at.% Ni for 2 h, and blending the resulting mixture with 40 vol.% NaCl powders for an additional 2 h. The upper layer is made by mixing near-equiatomic NiTi and Nb powders to obtain a eutectic composition of 74 at.% NiTi-26 at.% Nb (Ref 9), with the proportion of Nb (in the upper, eutectic layer) to overall NiTi (in both the upper, eutectic and lower, foam layers) being 3.1 at.% (5.3 wt.%) Nb. A double-layer pellet is formed by pouring the lower NiTi/Ni/NaCl mixture in a 12.7 mm die, adding the upper layer of NiTi/Nb mixture, and then cold pressing the two layers simultaneously with a pressure of 350 MPa. The preform is then heated under high vacuum in two stages: 1135 °C for 15 h, followed by 1185 °C for 10 h. The preform 2a with two layers had dimensions (12.7 mm in diameter, 10 mm in height) approximately the same as the perform 1 made by the simpler mixing method. To demonstrate the effect of process parameters on pore structure, another specimen labeled 2b was prepared by the double-layer procedure with the following

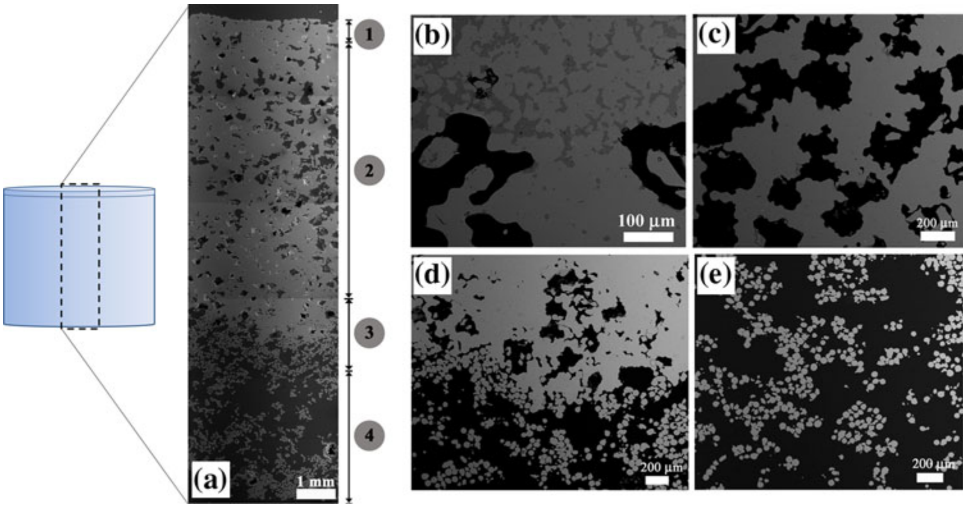

Fig. 3 SEM micrographs showing (a) a vertical cross section of foam 2b consisting of four regions (1-4); and high magnification images showing: (b) the interface between the eutectic layer (1) and foam layer (2); (c) the region (2) of full strut densification by eutectic infiltration; (d) the transition between the high and low densification regions (2-3); and (e) the region of poor densification (4) without eutectic infiltration

parameters: a composition in the NiTi/Nb layer of 86 at.% NiTi-14 at.% Nb (hypoeutectic), a NaCl volume fraction of 60%, and a sintering temperature of 1195 °C.

Cross sections of the sintered specimens were mounted in epoxy resin, polished with 320 μm SiC paper, 9 μm diamond paste, and 0.05 μm alumina paste, and imaged with a SEM equipped with energy dispersive x-ray (EDX) analysis.

3. Results and Discussion

The microstructure of foam 1 is shown in Fig. 2: it consists of macropores, 100-400 μm in diameter, surrounded by struts of poorly sintered NiTi powders. As expected, the macropores reflect the shape of the NaCl space-holders which were removed by evaporation during the sintering process (Ref 6). The micropores between the clearly distinguishable NiTi powders forming the foam struts and the lack of transient liquid phase are, however, unexpected because the processing temperature (1185 °C) was sufficient for the NiTi-Nb eutectic liquid to form. The low level of NiTi powder densification is comparable to that seen in the previous study (Ref 7), where pre-alloyed NiTi powders are sintered without Nb powders. The transformation temperatures measured by differential scanning calorimetry are equivalent to those of pre-alloyed NiTi with no additional Ni or Nb. Therefore, the procedure where Nb is used to densify foam struts of near-equiatomic prealloyed NiTi powder (Ref 7) does not transfer to NiTi foams to which Ni powders were added. This can be explained by considering the Ni-Nb phase diagram showing the intermetallic phases Ni_6Nb_7 and Ni_3Nb (Ref 10): it appears that the elemental Ni and Nb powders added to the NiTi-NaCl mixture did not react with NiTi upon heating, but rather reacted with each other to form one or more of the stable intermetallic phases Ni_6Nb_7 or Ni_3Nb. This prevented the formation of either Ni-rich NiTi compositions (Ni diffusing into NiTi) or a transient eutectic phase (Nb reacting with NiTi) and caused poor NiTi densification at elevated temperature. It is, however, expected that using pre-alloyed Ni-rich NiTi (rather than adding Ni powder to pre-alloyed near-equiatomic NiTi as done here) would result in densification with Nb addition. In fact, Grummon et al. (Ref 9) used Nb powder to successfully join Ni-rich NiTi strips.

Since interaction between elemental Ni and Nb must be avoided, the preforms (2a and 2b) in the second method was designed such that Nb and Ni were separated physically and functionally. Niobium without Ni was used in the upper layer where NiTi and Nb were mixed at the near eutectic composition to create a liquid at the processing temperature; this liquid then infiltrated the lower layer, which contained Ni without Nb to create a Ni-rich NiTi composition by diffusion prior to infiltration. Two consecutive heat treatments were designed to achieve these two separate goals. The first temperature (1135 °C) was chosen to promote interdiffusion between NiTi and Ni powders in the lower layer to form a homogeneous Ni-rich NiTi composition, while evaporating the NaCl to create a porous structure (NaCl has a boiling point at ambient pressure of 1413 °C but it sublimates readily in vacuum above its melting point of 801 °C; Ref 11). The first temperature (1135 °C) was below the Nb-NiTi eutectic temperature (~1170 °C; Ref 9) so that no liquid was formed in the upper layer. The second temperature (1185 °C) was then used to melt the upper layer into a Nb-NiTi eutectic liquid (for perform 2a). This liquid then wicked into the lower layer, aided by gravity, and filled the micropores between the Ni-rich NiTi powders without filling the macropores created by the evaporation of the NaCl powders.

Figure 3 shows a representative vertical cross section (12 mm in height) of foam 2b, produced by the double-layer method. The porosity was ~40%, and the angular macropores had sizes of 100-400 μm. These pore characteristics can be controlled by the amount, shape, and size of NaCl. The porous structure was inhomogeneous and divided into two main sections: a region without micropores which was infiltrated by the eutectic liquid, reaching from the top of the sample to a depth of 8-mm (labeled Region 2 in Fig. 3), and one of incomplete NiTi densification, with visibly distinct spherical NiTi particles and micropores, reaching from 8 mm depth to the bottom of the sample (labeled Region 4). The overall structure

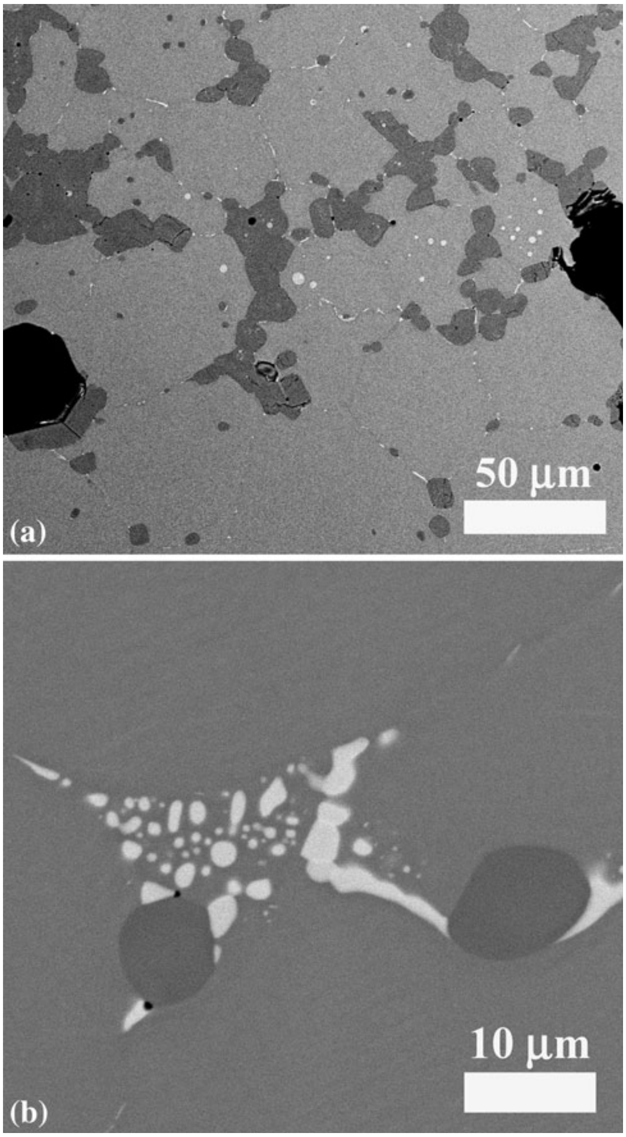

Fig. 4 SEM micrographs showing the microstructure of foam 2b: (a) at the interface between the upper (1) and lower (2) layers (the dark phase is a Ti-rich phase, the gray phase is the Ni-rich NiTi powders and NiTi eutectic, and the white phase is the Nb in the eutectic) and (b) within the foam layer (2), showing the eutectic phase and two Ti-rich particles filling the space between NiTi powders

implies that a sufficiently strong NiTi network was formed by sintering to avoid perform collapse when NaCl sublimated. The microstructure in Region 2 is similar to that of foam NTN40 in our previous study (Ref 7), where in situ transient liquid (NiTi-Nb) sintering occurred within NiTi struts (without Ni additions), while that in Region 4 is poorly densified like the structure of foam 1 (Fig. 2). The sharp transition from high (Region 4) to poor densification (Region 2) is evidence of an infiltration front, with the eutectic liquid formed in the upper layer wicking into, and enhancing densification of, the porous Ni-rich NiTi in the lower layer. During the gravity-assisted infiltration through the porous structure, capillary forces in the small channels between Ni-rich NiTi particles were sufficient to keep the liquid within the metal struts, preventing spilling into, and filling of, the macropores. Hence, the desirable macropores produced by NaCl evaporation were maintained.

Incomplete infiltration of the liquid into the foam layer was probably not caused by interdiffusion of Nb and NiTi, even though the equilibrium state of the whole specimen (both layers) is solid at 1170 °C (Ref 9). Unlike in some other systems [e.g., NiAl (Ref 12) and TiAl (Ref 13)] where interdiffusion between solid and transient liquid phases governs and limits infiltration, Nb in the eutectic layer is chemically stable, and Nb diffusion in solid NiTi is much slower than infiltration. The depth of the full strut densification Region 2 was therefore primarily determined by processing factors affecting the volume of the eutectic liquid. For instance, a sufficient amount of eutectic liquid supplied from the upper layer (i.e., an appropriate composition in the eutectic layer, and an appropriate proportion of eutectic layer to foam layer volumes) and a sufficiently high temperature (to ensure sufficient liquid is formed) will increase the depth of the full densification region. In addition, a foam layer having sufficiently high and uniform particle packing density would be useful, as this leads to higher capillary forces which enhance the wicking process.

The composition of the upper layer of foam 2b is NiTi-14 at.%Nb, a hypoeutectic composition consisting of about half liquid phase and half NiTi-rich solid solution at the processing temperature of 1185 °C. As observed in Region 1 of Fig. 3 and in Fig. 4(a), the majority of the solidified upper layer was occupied by the NiTi-rich solid phase (light gray, similar to the NiTi in the foam layer 2), with relatively little solidified eutectic liquid (white) remaining. This suggests that, as expected, most of the liquid formed in the upper layer wicked into the NiTi foam layer beneath. The flat interface between the two layers 1 and 2 suggests that erosion due to interdiffusion between the liquid layer and the underlying solid layer was minimal. At NiTi powder boundaries in the interface and foam layers (2 and 3), small volumes of eutectic phase are present, containing large (∼10 μm) faceted precipitates, which were identified in our previous study as a $NiTi_2$-rich phase (Ref 7). More eutectic regions are visible, bonding the NiTi particles with each other in the foam layer (Fig. 4b). According to the NiTi-Nb phase diagram (Ref 9), the targeted composition of the upper layer could be near the eutectic composition where the alloy is entirely

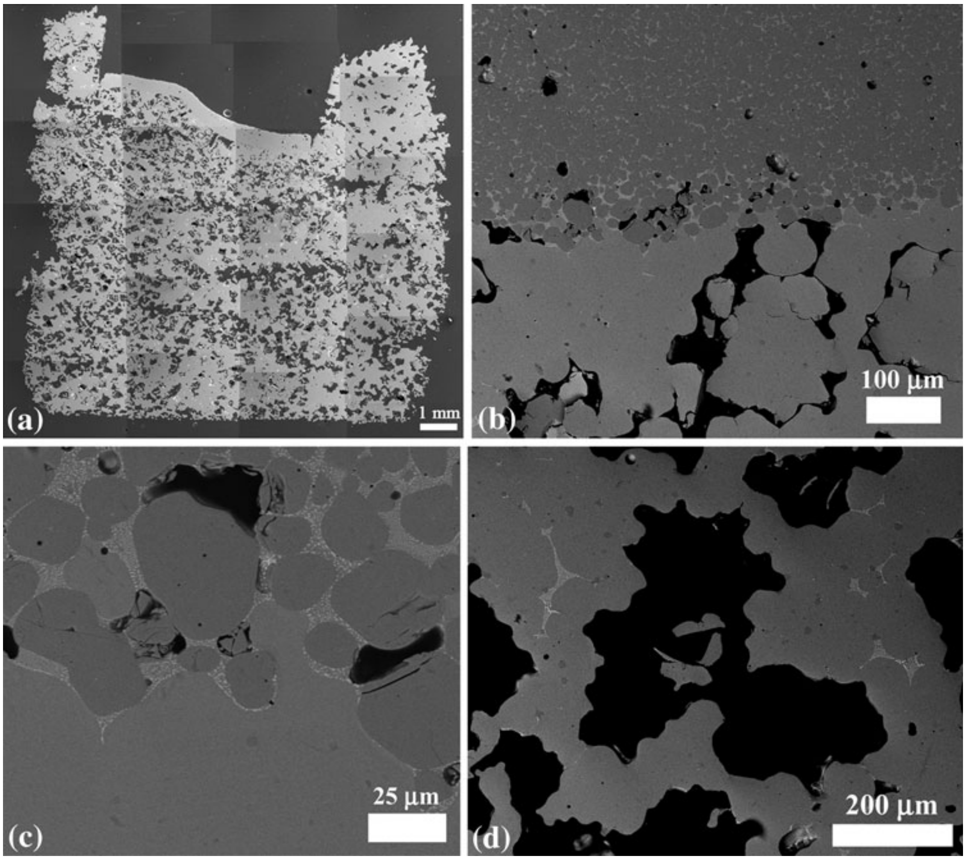

Fig. 5 SEM micrographs of (a) a vertical cross section of foam 2a showing full infiltration throughout the perform; and high magnification images representing; (b, c) the interface between the eutectic layer (near top of foam) and the foam layer at two magnifications and (d) high strut densification region. Pores are black, NiTi is gray, the Nb in the eutectic phase is white, and the round darker gray shapes are Ti-rich phases

liquid at a temperature above the eutectic point. Compositions at or below eutectic are preferred for the upper layer, in contrast to hypereutectic compositions where further dissolution of NiTi is required by the Nb-rich liquid infiltrated between the NiTi powders when the temperature drops to the eutectic temperature.

To demonstrate optimization of the double-layer process, foam 2a was produced by the same procedure as foam 2b, but with a eutectic composition (26 at.% Nb versus 14 at.% Nb) in the upper layer, a higher sintering temperature (1195 °C versus 1185 °C), and a higher fraction of NaCl space-holders (60 vol.% versus 40 vol.%). As shown in Fig. 5(a)-(d), a structure similar to foam 2a was obtained, except with full strut densification throughout the preform. Because of its eutectic composition, the upper layer was fully transformed to eutectic liquid at 1185 °C, providing about twice the volume of liquid present in foam 2a for wicking into the lower foam layer. The increase in temperature by 10 K also reduced the viscosity of the liquid, accelerating the wicking process. Finally, a lower NiTi strut volume was present, because of the higher fraction of NaCl space-holders.

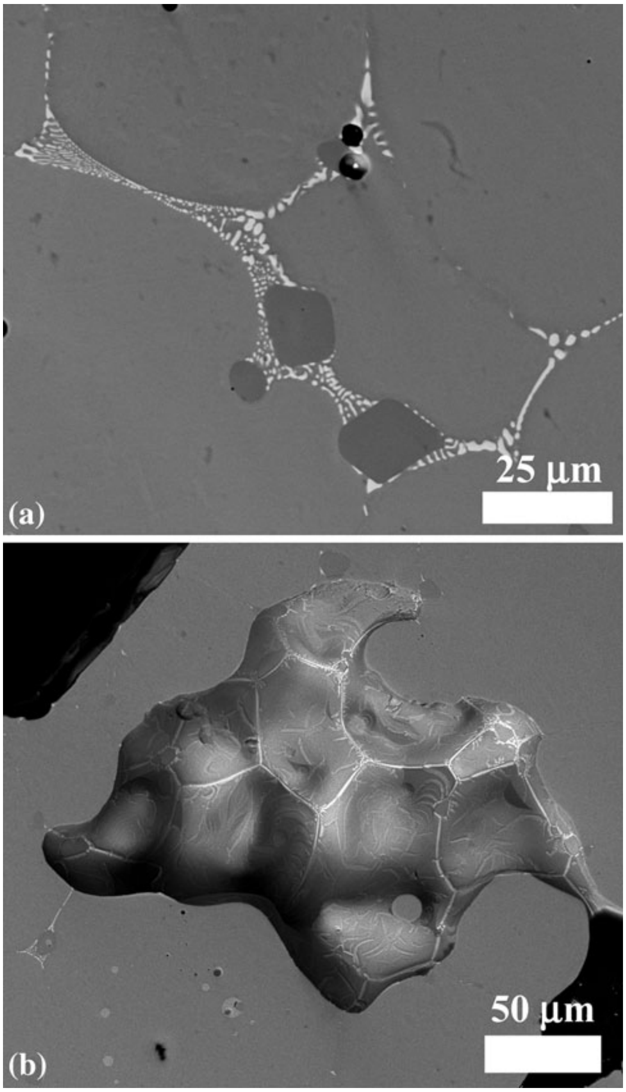

Fig. 6 SEM micrographs of interparticle boundaries in foam 2a on (a) polished surface and (b) inside a pore; showing eutectic region (with white Nb particles) and blocky Ti-rich phase (dark)

The total Nb amount in foam 2a is 8 wt.%, which is greater than the 6 wt.% Nb in foam 2b. Because of the eutectic feature, the liquid composition is similar in each case but foam 2b has a greater fraction of liquid. However, the quantity of eutectic liquid in a given volume of the NiTi foam layer is given by the amount of microporosity available to be filled, which is again similar between the foams. Thus, the composition and fraction of the liquid phase that acts to densify the foam struts after solidification are similar, despite the significant differences in overall processing and the foam properties are also expected to be similar.

The eutectic phase formed on the upper layer is visible in Fig. 4(b) as lamellar eutectic white (high Z) Nb particles within a NiTi matrix, surrounding large round phase that are darker (i.e., with lower Z) than the NiTi powders and are thus Ti-rich (most probably $NiTi_2$). The presence of this Ti-rich phase, also observed in a $Ni_{45}Ti_{45}Nb_{10}$ alloy with lower Nb:NiTi ratio (Ref 14), suggests that the amount of Nb participating in liquid formation was decreased after early eutectic liquid was formed and drained out. In the lower layer, the eutectic phase and blocky Ti-rich precipitates appear at the interfaces of NiTi powders throughout, as expected from previous result (Ref 7). As a consequence, the densification of NiTi struts was of good quality, as shown both within a strut (Fig. 6a) and in an inner pore (Fig. 6b).

The overall shape of foam 2a is, however, distorted in its upper region (Fig. 5a). A possible reason is the fluctuation in the in situ composition of the upper layer, especially toward the hypereutectic composition. At a temperature 25 K above the 1170 °C eutectic temperature (possibly within the furnace temperature variation), the NiTi foam layer could be partially dissolved into the eutectic. The liquid formed in the upper layer would then have been drawn inward to the center of the crucible by surface tension before infiltrating through the porous structure, and so the NiTi foam layer beneath the center was weighed by liquid and dissolved preferentially, leading to slumping. Further adjustments in processing to the double-layer method are likely to lead to higher macroporosity, shorter processing times, and larger, more uniform sample size.

4. Conclusions

A novel method is developed for producing porous Ni-rich NiTi by combining a space holder method to control the features of the porous structure and eutectic liquid brazing of NiTi powders to ensure high densification of NiTi struts made of pre-alloyed, near-equiatomic NiTi powders. The method consists of (i) mixing pre-alloyed NiTi powders with Ni addition and NaCl space-holders into a first blend; (ii) mixing Nb as a transient liquid phase sintering agent into the pre-alloyed NiTi powders to form a second blend; (iii) pressing the two blends to form a two-layer powder compact; (iv) sintering the compact at a temperature below the Nb-NiTi eutectic point to evaporate the NaCl in the lower layer, diffuse the Ni into the NiTi powders and lightly sinter the NiTi powders; and (v) heating the compact to a temperature above the eutectic point, to create a eutectic liquid in the upper layer that then wicks into the space between the NiTi powders in the lower layer to enhance their densification.

The key strategy of the method is the physical and functional separation of Nb (in the upper liquid layer) and Ni (in the lower foam mixture layer), which allows Nb to form a eutectic liquid with NiTi before infiltrating the foam layer where a Ni-rich composition has been previously created by diffusion of Ni into NiTi. Therefore, the double layering offers a separate control of NiTi composition (by Ni addition), NiTi densification (by transient liquid phase sintering), and macropore characteristics (by NaCl space-holder addition). This relies on the finding that the transient NiTi-Nb liquid infiltrates through capillary forces the small channels between the partially sintered, Ni-rich NiTi particles, but without filling the macropores generated by the space-holders. Full strut densification of the NiTi foam can be achieved using a sufficient amount of eutectic liquid produced from the NiTi-Nb mixture in the upper layer, thus allowing the production of large foam parts of arbitrary shape for biomedical and actuation applications.

Acknowledgments

This research was supported by the United States National Science Foundation (Grant DMR-0505772). AB also gratefully acknowledges support, through the Faculty of Engineering, Kasetsart University (Thailand), and technical advice from Dr. Alan Brothers.

References

1. A. Bansiddhi, T. Sargeant, S. Stupp, and D.C. Dunand, Porous NiTi for Bone Implants: A Review, *Acta Biomater.*, 2008, **4**(4), p 773–782
2. T. Aydogmus and S. Bor, Processing of Porous TiNi Alloys Using Magnesium as Space Holder, *J. Alloys Compd.*, 2009, **478**(1–2), p 705–710
3. M. Kohl, T. Habijan, M. Bram, H.P. Buchkremer, D. Stover, and M. Koller, Powder Metallurgical Near-Net-Shape Fabrication of Porous NiTi Shape Memory Alloys for Use as Long-Term Implants by the Combination of the Metal Injection Molding Process with the Space-Holder Technique, *Adv. Eng. Mater.*, 2009, **11**(12), p 959–968
4. D.S. Li, Y.P. Zhang, X. Ma, and X.P. Zhang, Space-Holder Engineered Porous NiTi Shape Memory Alloys with Improved Pore Characteristics and Mechanical Properties, *J. Alloys Compd.*, 2009, **474**(1–2), p L1–L5
5. X.K. Zhao, H.B. Sun, L. Lan, J.H. Huang, H. Zhang, and Y. Wang, Pore structures of High-Porosity NiTi Alloys Made from Elemental Powders with NaCl Temporary Space-Holders, *Mater. Lett.*, 2009, **63**(28), p 2402–2404
6. A. Bansiddhi and D.C. Dunand, Shape-Memory NiTi Foams Produced by Replication of NaCl Space-Holders, *Acta Biomater.*, 2008, **4**(6), p 1996–2007
7. A. Bansiddhi and D.C. Dunand, Shape-Memory NiTi-Nb Foams, *J. Mater. Res.*, 2009, **24**(6), p 2107–2117
8. H. Matsuno, A. Yokoyama, F. Watari, M. Uo, and T. Kawasaki, Biocompatibility and Osteogenesis of Refractory Metal Implants, Titanium, Hafnium, Niobium, Tantalum and Rhenium, *Biomaterials*, 2001, **22**(11), p 1253–1262
9. D.S. Grummon, J.A. Shaw, and J. Foltz, Fabrication of Cellular Shape Memory Alloy Materials by Reactive Eutectic Brazing Using Niobium, *Mater. Sci. Eng. A Struct. Mater.*, 2006, **438**, p 1113–1118
10. H. Baker, Ed., Alloy Phase Diagrams, *ASM Handbook*, Vol 3, 1992, p 2.304
11. P. Patnaik, *Handbook of Inorganic Chemicals*, McGraw-Hill, New York, 2003
12. D.C. Dunand, J.L. Sommer, and A. Mortensen, Synthesis of Bulk and Reinforced Nickel Aluminides by Reactive Infiltration, *Metall. Trans.*, 1993, **24A**, p 2161–2170
13. A. Lorenz, E. Sachs, and S. Allen, Freeze-off Limits in Transient Liquid-Phase Infiltration, *Mater. Sci. Eng. A Phys. Metall. Mater. Sci.*, 2004, **35A**(2), p 641–653
14. V.A. Udovenko, P.L. Potapov, S.D. Prokoshkin, I.Y. Khmelevskaya, V.Y. Abramov, and Y.V. Blinov, A Study of the Functional Properties of Alloy Ti-45%Ni-10%Nb with Wide Hysteresis of the Martensitic Transformation, *Met. Sci. Heat Treat.*, 2000, **42**(9–10), p 353–356