Niobium Wires as Space Holder and Sintering Aid for Porous NiTi**

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When NiTi powder compacts containing Nb wires are heated above 1 170 °C, each Nb wire reacts with adjacent NiTi powders to form a eutectic liquid which wicks into the space between the remaining NiTi powders. This creates a macropore at the location of the Nb wire while eliminating the microporosity between NiTi powders which is filled with a NiTi/Nb eutectic phase after solidification. This novel method produces – in a single step and without applied pressure – a dense NiTi matrix with elongated pores suitable for shape memory or superelastic applications such as bone implants, dampeners and actuators.

Several processing methods exist to create porous NiTi (nitinol) that fulfills engineering applications (e.g., as dampener or actuator) or biomedical requirements (e.g., as implant).[1] Porous NiTi has an unusual combination of properties associated with its porous structure (i.e., low density, low stiffness, high permeability) and the alloy itself (i.e., high corrosion resistance, high strength, excellent biocompatibility, and shape recovery), making it uniquely suited as bone implant. An attractive strategy for producing porous NiTi is based on the combination of temporary space-holders with powder metallurgy methods to achieve control over pore structure and fraction. The most commonly used temporary space-holders for NiTi are non-metallic substances such as polymer, saccharose,[2] NaCl,[2,3] urea, and NH$_4$CO$_3$,[4] which evaporate during or after the powder consolidation process. These pore-forming space-holders can produce > 30% macroporosity with a 100–400 μm size range optimal for osseo-integration; however, the final microstructure often also displays microporosity with micron- to submicron size due to the Kirkendall effect or insufficient powder densification, which tends to weaken the alloy. Many

consolidation techniques such as hot isostatic pressing[3] or the use of elemental Ni and Ti powders[1] have been applied to reduce microporosity, with a trade-off in expense or undesirable intermetallic phases, respectively. In our recent studies[5,6] Nb was identified as a densification enhancer in porous NiTi:mixed NiTi/Nb powders react to create a small volume fraction of wetting eutectic liquid which fills the microporosity between the remaining NiTi powders while NaCl is used as a space-holder to create macropores. The NiTi–Nb solid alloy present after solidification was reported as biocompatible[7] with good damping behavior.[8]

In the present work, a novel fabrication strategy for porous NiTi–Nb is demonstrated, based on, but distinct from, our earlier method using NaCl.[5,6] We use here niobium in discontinuous wire form as both space-holder and densification enhancer for NiTi powders. Metallic space-holders have been used previously to create porous alloys, but they have never, to our knowledge, been used also as densification enhancer. For instance, NiTi powders were densified with Mg powders space-holders which evaporated during consolidation[9] and Ti,[10] Ti-6Al-4V[11] or NiTi powders[12] were densified with steel wires which were removed electrochemically to create elongated pores.

The Nb wires in the present work were expected to completely react with the surrounding NiTi powders to form a eutectic liquid which then wicked through available capillary channels within the NiTi powder compact to densify it, while leaving the previously occupied wire spaces empty as elongated pores. One of the advantages of the NiTi–Nb system for such a process is the ability to create this transient eutectic liquid at temperatures below both the NiTi and Nb melting points, which reduces production cost and energy use. Another advantage is that the stable eutectic liquid can wick through capillary channels without appreciable reaction with, or dissolution of,

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NiTi. The liquid can then be solidified by reducing the temperature after the infiltration, rather than relying on dissolution or chemical reaction during the infiltration to reach equilibrium. This stands in contrast to a study,[13] where NiAl microchannels were produced in a Ni powder compact by melting Al wires; in that case, rapid solid NiAl formation between liquid Al and the Ni powders limited penetration of the liquid through the surrounding capillary volumes.

Experimental

A first sample (labeled 1a) was prepared by embedding four Nb wires (10 mm in length, 0.125 mm in diameter and with 99.9% purity, procured from Advent Research Materials Ltd., Oxford, England) within a bed of 3 g NiTi powders (48.6 at% Ni, sieved to 44–63 μm in size and procured from Specials Metals, MA), arranging them parallel to one another in a horizontal plane with a spacing of ≈2 mm. A 12.7 mm diameter stainless steel die was first filled with 1.5 g of NiTi powder and cold pressed at 100 MPa. The four Nb wires were then placed individually on top of the NiTi compact, covered up with another 1.5 g of NiTi powder, and the compact was pressed again to the pressure of 350 MPa to a final height of 5 mm. The compact was then sintered in a high vacuum furnace at 1 185 °C for 10 h with a heating rate of 7 °C · min^{-1}, and then furnace cooled to room temperature. Another compact with the same dimensions was prepared using the same procedure, except with six layers each containing seven parallel Nb wires per layer. The total amount of Nb in this second sample (labeled 1b) was 1 wt% Nb (10 times higher than that of sample 1a). Two additional samples were prepared using the same procedure as for sample 1b but with slight modification in NiTi powder; pre-mixed with 1 at% Nb powders (sample 1c) and with Ni powders for an overall Ti-50.8 at% Ni composition (sample 1d).

Porous NiTi containing 3D-connected wires was prepared by mixing for 2 h in a tumbler Nb chopped wires (0.125 mm diameter, 0.5–1 mm in length) and the same pre-alloyed NiTi powder in the ratio of 3.3 wt% Nb to 96.7 wt% NiTi, corresponding to ≈200 cm of wire in total. The NiTi powders containing randomly oriented chopped Nb wires were die pressed at 350 MPa into a 12.7-mm diameter, 8 mm-tall preform which was then sintered at 1 185 °C for 10 h using the same procedure described above, resulting in sample 2a. Another specimen (labeled 2b) containing randomly oriented Nb wires with a larger, 0.25 mm diameter in the same volume fraction was also prepared by the same procedure for comparison.

The densified compacts were sectioned with a low speed diamond saw, and cross-sections were mounted in epoxy, polished with 320 μm grit paper, lapped with 9 μm, and 0.5 μm polishing solutions and observed by optical and scanning electron microscopy (SEM). Porosity measurement was done by SEM image analysis. Phase transformation behavior for representative specimens was measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 (Shelton, CT) with a heating and cooling rate of 10 K · min^{-1} under nitrogen cover gas. Two DSC cycles (ranging from 60 to 170 °C) were performed consecutively for each sample, and the second cycle was used to determine the transformation enthalpy (from integration of the peaks) and the phase-transformation temperatures (A_s, A_f, M_s, and M_f, determined using the intercepts of lines tangent to the highest slopes of the peaks with the baseline).

Results and Discussion

Aligned Elongated Porosity

The microstructure of porous sample 1a is shown in Figure 1(a). The space previously occupied by the cross-section of a Nb wire is now visible as a pore near the center of
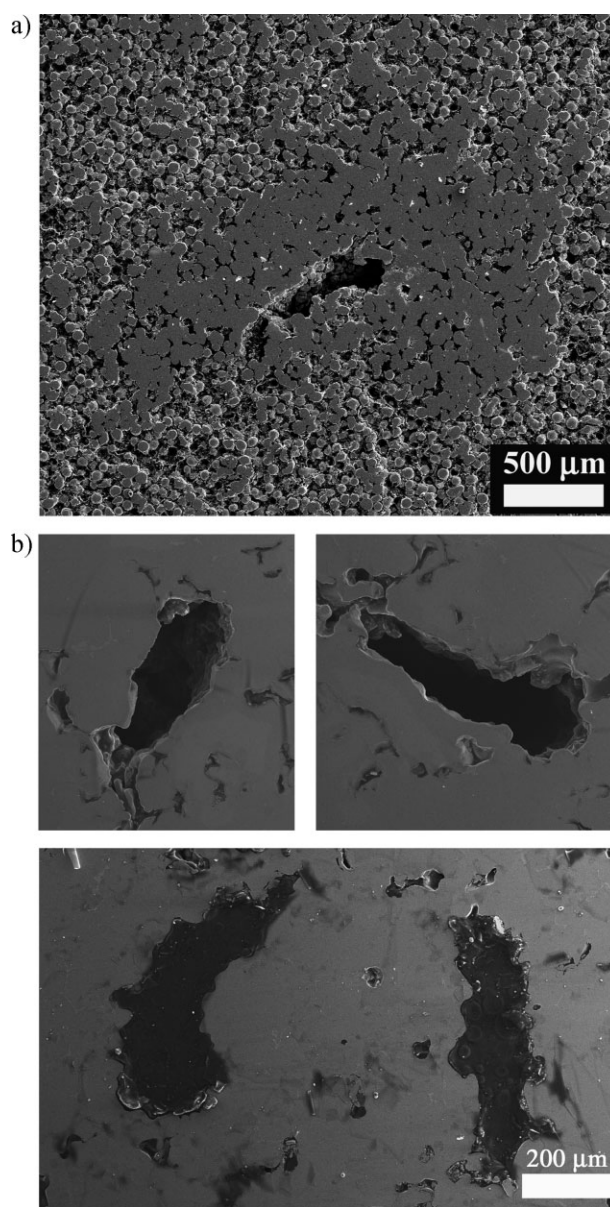

Fig. 1. SEM micrographs of porous NiTi (a) sample 1a, with widely spaced Nb wires and (b) sample 1b with closely spaced Nb wires.
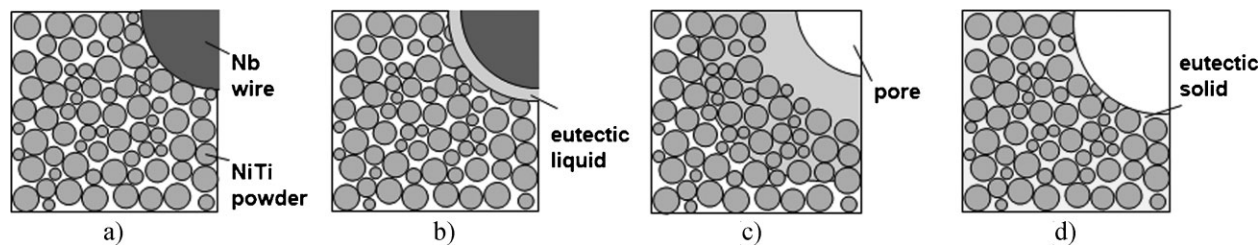
Fig. 2. Schematic of steps occurring during transient liquid formation by reaction between a Nb wire (shown as a quarter of a cross-section) and surrounding NiTi powders: the liquid wicks and infiltrates the space between the NiTi powders, thus creating an empty macropore and filling the micropores between the NiTi powders.

the image, and two features are apparent: (i) the shape of the pore is heavily distorted from the original circular shape of the wire; and (ii) the overall cross-sectional area of the pore is larger than that of the wire. The former may be due to local rearrangement of the NiTi powders during melting of the Nb combined with the effects of sectioning the sample slightly off-axis, while the latter is due to formation of the eutectic liquid (26 at% Nb-74 at% NiTi),[14] which requires a reaction between the wire and the surrounding NiTi powders which are therefore consumed. A densified region, extending over a $\approx 500 \, \mu m$ distance from the pore surface, shows the infiltrating distance of the eutectic phase through the NiTi interparticle spaces. Low densification, manifest as visible individual NiTi powders, is observed in the rest of the porous body. The partial densification implies that insufficient eutectic liquid formed in the NiTi body, i.e., that the number of Nb wires was too low this was by design, so as to understand the extent of the infiltration of the eutectic liquid without overlap from neighboring Nb wires. A schematic representation of the ideal mechanism expected from this technique is shown in Figure 2, where sufficient liquid is produced to densify all the NiTi matrix.

In sample 1b, where the number of Nb wires in the pellet was increased and space between wires was decreased, high densification around pores was present [Figure 1(b)]. However, the cross-sections of the pores were still highly elongated ($\approx 500 \, \mu m$ in length) along seemingly random directions, rather than being symmetric or circular/ellipsoidal as assumed in the ideal case. The pore axes of elongation seem not to be influenced by gravity, but possibly reflect an anisotropic wicking/reaction process. As the temperature reached the eutectic (1 170 °C), a layer of transient liquid phase was formed between the surface of each Nb wire and the neighboring NiTi powders, and was drawn out by capillary forces to fill the adjacent micropore channels (as illustrated schematically in Figure 2). The degree of infiltration at any point (or in any direction) depends sensitively on the magnitude of these capillary forces between compacted NiTi particles, which increases with packing factor. It is therefore likely that the layer of liquid was drawn preferentially in directions of high packing (or high surface tension). More uniform packing of NiTi powder may therefore promote a more homogeneous microstructure and more regular pore shapes. It is worth noting that using a eutectic system where the liquid formation temperature lies below the melting points

of both substances (NiTi and Nb, in this case) also promotes a homogeneous pore structure, by avoiding the microstructure collapse that can be triggered by the liquid phases in other systems such as NiAl.

The wicking process could end before complete solidification if driving forces, such as the gradient of composition, capillary forces, or temperature, are removed. Figure 3
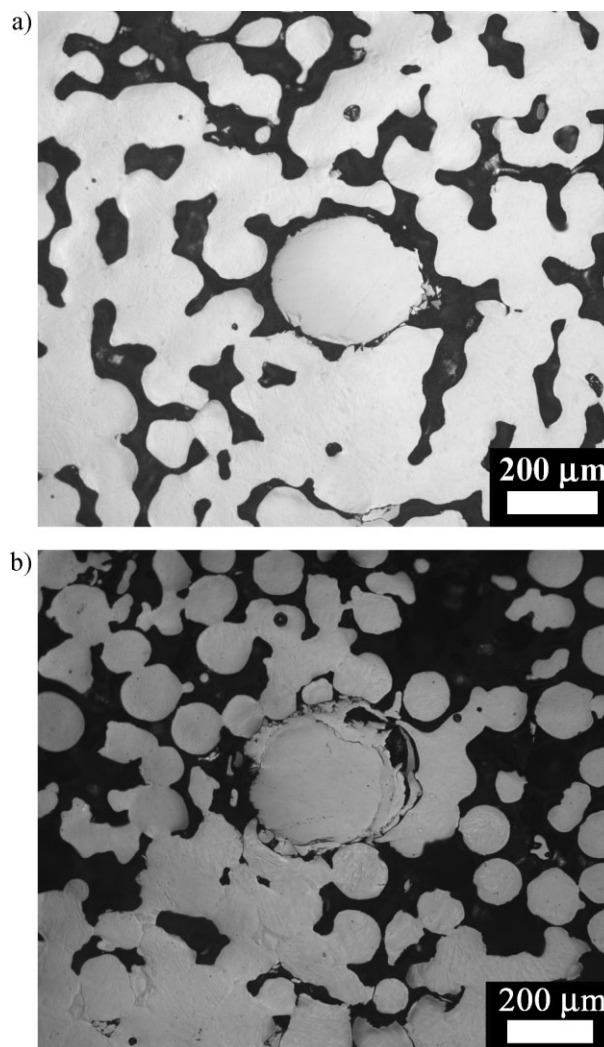

Fig. 3. Optical micrographs of porous NiTi samples made with NiTi powders with additions of (a) Nb powders (sample 1c) and (b) Ni powders (sample 1d). The round white feature near the center of each image is the cross-section of an undissolved Nb wire within the mixed powder matrix.

presents effect of Nb powders [Figure 3(a)] and Ni powders [Figure 3(b)] additions to the NiTi powders. These powder additions reduced the driving force of the reaction between NiTi powders and Nb wires, the Nb wires were left unreacted in both cases. The dispersed Nb powders readily formed *in situ* eutectic (like in our previous work) with NiTi which wicked through microporosity and abruptly decreased capillary forces. According to the Ni–Nb phase diagram,[15] the Ni powders tended to form stable Ni–Nb intermetallics with the Nb wires at lower temperature, thus preventing the NiTi–Nb reaction in sample 1d.

Three-Dimensionally Connected Porosity

To create three-dimensional connectivity and improve the packing of NiTi powders, Nb chopped wires with 0.125 mm diameter were used to produce porous NiTi. The resulting cross-sections [Figure 4(a)] reveals elongated macropores with projected width of 200–300 μm and lengths of 0.5–1 mm, along with a few micropores 5–10 μm in size. The total porosity was 30% (90% of which was open). As for the previous samples, macropores were produced by the dissolution of the Nb wire space-holders above the eutectic temperature, as well as the accompanying dissolution of some surrounding NiTi powders. Well-densified NiTi matrix was achieved with the help of the eutectic phase [the white features in Figure 4(b–d)]

bonding the NiTi particles together. The residual micropores may result from incomplete infiltration, which could be eliminated by an increase in sintering time, sintering temperature and/or amount of Nb chopped wires. The obtained macroporosity of ≈30% was in agreement with the previous result [Figure 2(b)] that a given volume of Nb space-holder can result in a much greater pore volume. In this case, the amount of Nb chopped wires used to achieve a 1.8 at% Nb–98.2 at% NiTi composition provided ≈2 vol% Nb space-holders to the specimen volume, but produced ≈15 times as much porosity. The results suggest that larger pore sizes and higher porosities could be achieved by increasing the diameter and number of equal-length cut Nb wires, respectively. An example of this approach is provided in Fig. 4(c) and (d), showing that sample 2b, produced using Nb wires with larger diameter (0.25 vs. 0.125 mm), indeed results in larger pores. However, packing limitations between the Nb wires and NiTi powders will determine the practical limits of tailoring pore characteristics (porosity, pore size, pore shape) with this method.

The porous NiTi specimen 2a produced with 0.125 mm Nb wires exhibits phase transformation temperatures ($A_s = 44\,°C$, $A_f = 75\,°C$, $M_s = 30\,°C$, $M_f = -25\,°C$, Figure 5) compatible with shape-memory properties at ambient and body temperature. This confirms that Nb can be successfully used in the
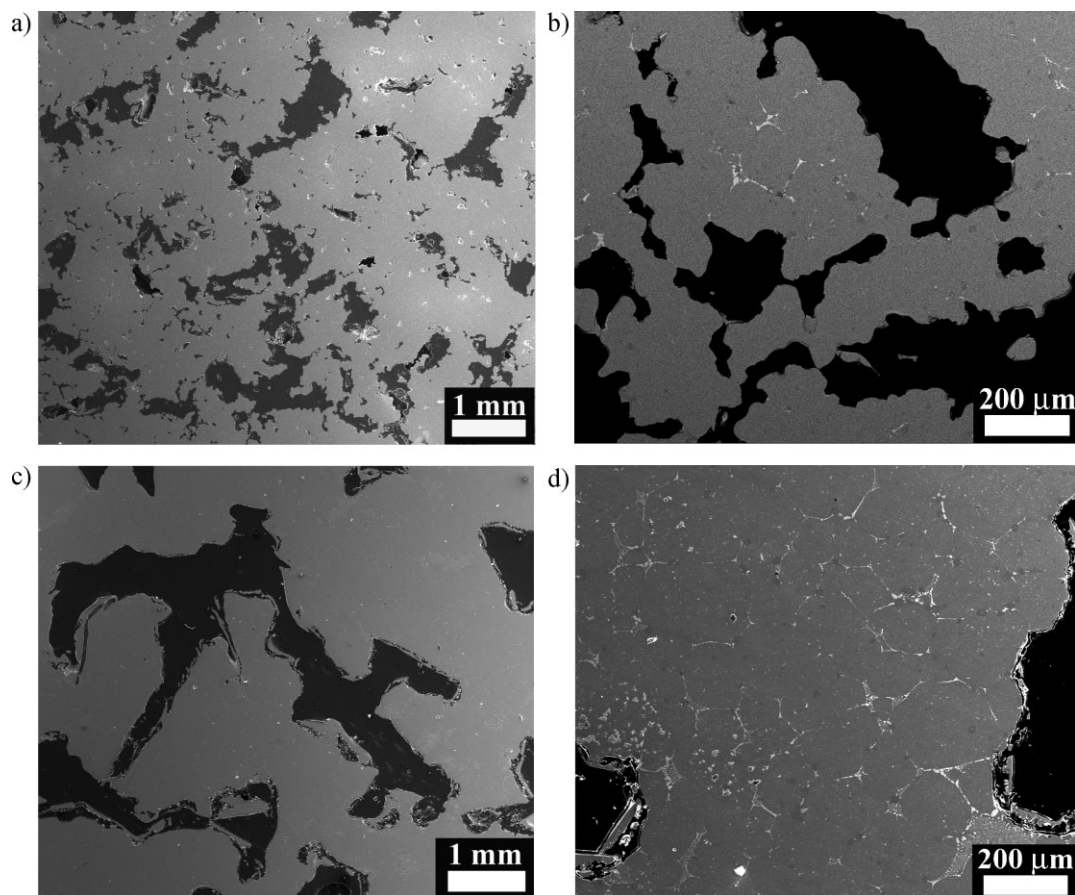

Fig. 4. SEM micrographs of porous NiTi illustrating that the size of the macropores is related to the initial Nb wire diameter: (a–b) sample 2a created with 0.125 mm diameter Nb wires; (c–d) sample 2b created with 0.25 mm diameter Nb wires.
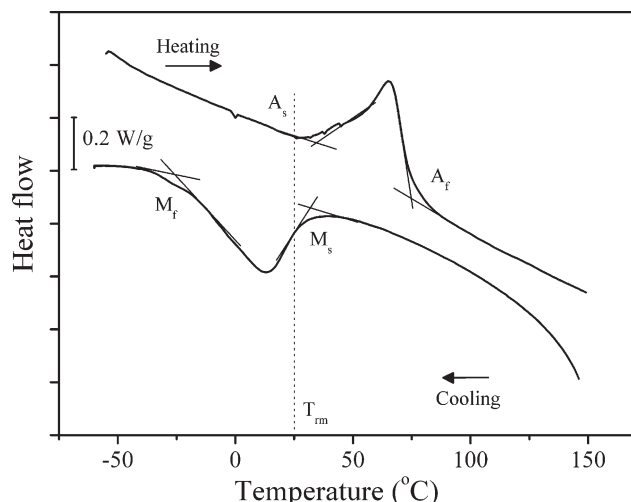
Fig. 5. DSC curve for porous NiTi sample 2a, showing transformation temperatures consistent with the shape memory effect at room temperature (represented as a vertical dashed line).

processing of porous NiTi as both a pore creator and densification enhancer, without sacrificing the shape memory effect of NiTi (similar result to those produced in the previous work were reported for NiTi with NaCl as space-holders and Nb powders as densifier).[5]

Conclusions

A novel, single-step technique is developed that provides an effective means for producing, at relatively low temperatures and without applied pressure, porous NiTi with elongated pores for potential application as actuators or biomedical implants. Above 1 170 °C, Nb wires react fully with NiTi powders in which they are embedded to form a NiTi–Nb eutectic liquid. The liquid wicks into the NiTi compact, eliminating undesirable microporosity between the NiTi powders and leaving elongated macroporosity at the location of the wires. Several interesting areas remain to be investigated to further develop this method made possible by the low-melting, wetting NiTi–Nb eutectic; they include a better understanding of the physical mechanisms at play (reaction, infiltration, solidification) and the development of strategies for controlling pore characteristics (fraction, size, shape, aspect ratio, connectivity, and orientation).

[1]   A. Bansiddhi, T. D. Sargeant, S. I. Stupp, D. C. Dunand, *Acta Biomater.* **2008**, *4*, 773.

[2]   M. Kohl, T. Habijan, M. Bram, H. P. Buchkremer, D. Stover, M. Koller, *Adv. Eng. Mater.* **2009**, *11*, 959.

[3]   A. Bansiddhi, D. C. Dunand, *Acta Biomater.* **2008**, *4*, 1996.

[4]   D. S. Li, Y. P. Zhang, G. Eggeler, X. P. Zhang, *J. Alloys Compd.* **2009**, *470*, L1.

[5]   A. Bansiddhi, D. C. Dunand, *J. Mater. Res.* **2009**, *24*, 2107.

[6]   A. Bansiddhi, D. C. Dunand, *J. Mater. Eng. Perform.*, in press.

[7]   C. Li, Y. F. Zheng, L. C. Zhao, *Mater. Sci. Eng. A.* **2006**, *438*, 504.

[8]   F. Xiao, X. Q. Zhao, H. B. Xu, H. C. Jiang, L. J. Rong, *Acta Metall. Sinica* **2009**, *45*, 18.

[9]   T. Aydogmus, S. Bor, *J. Alloys Comp.* **2009**, *478*, 705.

[10]   P. J. Kwok, S. M. Oppenheimer, D. C. Dunand, *Adv. Eng. Mater.* **2008**, *10*, 820.

[11]   D. J. Jorgensen, D. C. Dunand, *Mater. Sci. Eng. A* **2010**, *527*, 849.

[12]   A. J. Neurohr, D. C. Dunand, *Acta Biomater*, in press.

[13]   T. Ohmi, N. Hayashi, M. Iguchi, *Mater. Trans.* **2008**, *49*, 2723.

[14]   D. S. Grummon, J. A. Shaw, J. Foltz, *Mater. Sci. Eng. A* **2006**, *438*, 1113.

[15]   H. Baker, in *Alloy Phase Diagrams, ASM Handbook*, Vol. 3, **1992**. ASM International, Materials Park, OH, USA.