THE MANUFACTURE OF NITI FOAMS

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ABSTRACT
Ongoing research is presented on processing of NiTi–based shape memory alloy (SMA) foams. The aim is to demonstrate a new class of materials that combine the advantages of light–weight metallic foams with the strain recovery and energy–dissipation capability of SMAs. There are a number of potential novel structural and biomedical applications that could be enabled by the unusual passive and active properties of such a material. This paper presents initial results on our attempt to fabricate functional prototype specimens using a polymeric foam precursor and a powder metallurgy process to produce NiTi foams with user–selected topology and relative density. It is shown that open–cell NiTi foams with relative density less than 5% can be produced with this technique. While definite martensitic transformational behavior has been achieved in the prototypes, the quality of the foams are found to be sensitive to the sintering temperature, the binder system employed, and the levels of interstitial contamination. Further work is needed before good superelastic and shape–memory properties can be demonstrated. Nevertheless, the current technique appears promising, since the method is capable of producing NiTi foam with a more regular structure and at a relative density nearly an order of magnitude less than other techniques currently used to produce porous NiTi.

INTRODUCTION
Structural polymeric foams are quite common and are used in many cushioning applications for packaging and for thermal insulation. Recent manufacturing advances have made it possible to create metallic foams, which are of increasing technological importance (see Gibson & Ashby, 1997; Ashby et al., 2000). In this paper we define foams as materials with an extreme degree of free space less than 10% dense, in contrast to simple porous materials that are typically 40 to 90% dense. Metallic foams can be produced in either two–dimensional honeycombs or three–dimensional open– or closed–cell configurations (see Fig. 1), depending on the manufacturing process. Open–cell foams consist of a network of thin ligaments joined at nodes that act as beam/torsion elements. Closed–cell foams, by contrast, are composed of intersecting polyhedra with the material forming thin shell elements. Both forms combine light weight and high specific stiffness properties that are suitable for a number of structurally efficient applications, such as sandwich cores. Manufacturing techniques are currently being developed that can produce complex geometries, and in the case of sandwich cores, include integral face plates. In overload conditions they can provide efficient energy absorption through the mechanisms of crushing and densification. These structures are initially stiff in compression, but once a critical load is reached they crush by buckling and collapse of the thin ligaments at a relatively constant load. In addition, providing cooling flow of gaseous or liquid materials throughout an open–cell foam provides an effective means of heat transfer, thereby making the foam multifunctional.

A variety of manufacturing approaches have been demonstrated to produce foams from conventional alloys, including inert gas blowing, mechanical stirring, or the introduction of outgassing agents into the molten metal before freezing. Aluminum is a particularly convenient choice for these processes, due to its

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low density and low melting point. Investment casting has also been used, in which the melt is poured into the interstices of particulate materials, like salt, which can then be dissolved away after freezing.

The ultimate objective of this work is to develop a new class of materials that combines the remarkable properties of a shape memory alloy (SMA) with the extremely sparse topology of a foam. SMAs, such as NiTi (or Nitinol), in wrought form exhibit two remarkable strain recovery properties, the \textit{shape memory effect} and \textit{superelasticity}. The first refers to an SMA’s ability to recover large mechanically-induced strains (up to 8\%) by moderate increases in temperature. The latter refers to the rubber–like, hysteretic strain recovery in somewhat higher temperature regimes. In each case, the underlying mechanism is a reversible martensitic transformation between solid-state phases that can be induced by changes in temperature or stress (see Fig. 2). The most technologically important SMA, near equiatomic NiTi, also has excellent structural properties, very good corrosion resistance, and long–term bio–compatibility, making it an attractive choice for many innovative structural applications (see Duerig \textit{et al.}, 1990; Otsuka & Wayman, 1998).

In concept, SMA foam materials have the potential to act as new adaptive structural elements, responding to changes in external loads and the thermal environment. Also, the superelastic properties of SMAs may be used to create light–weight, reusable energy absorbing materials, or highly damage–tolerant ‘self–repairing’ materials. A variety of novel applications may be envisioned for the material, such as impact–tolerant armor, vibration–isolation elements, adaptive skins and control surface elements, to name a few. The bio–compatibility and extreme porosity of a NiTi foam may also lend itself nicely to biomedical devices and implants.

We note the recent work of Thangaraj \textit{et al.} (2000); Lagoudas \textit{et al.} (2001) to produce and model porous NiTi specimens near 50\% relative density. Their approach used hot isostatic pressing (HIP) or sintering of elemental powders to produce a porous material. Chinese researchers have also produced porous NiTi by combustion synthesis (see Li \textit{et al.}, 2000). The porosity these achieved was relatively small and was random in nature, tending to lead to stress concentrations and incomplete strain recovery.

Our objective, by contrast, is to produce a lighter (5\% dense) NiTi foam with a user–selected and more regular open–cell structure, which will lead to better specific stiffness and improved strain recoverability. To the authors’ knowledge the manufacture of SMA foams that are less than 10\% dense has not yet been attempted. This paper addresses the first phase of our work to fabricate such materials.
SMA foam would create benefits well beyond those of conventional metal foams or of monolithic SMAs. It has been shown experimentally (Leo et al., 1993; Shaw & Kyriakides, 1995, 1997) that the “rate-effect” in SMAs is not due to the usual visco-elastic phenomena, but rather, involves a strong interaction between the latent heat of transformation and the extreme sensitivity of the transformation stress to temperature (as described by the Clausius–Clapeyron relation). In other words, self-heating or self-cooling during a stress-induced martensitic transformation creates a feedback loop that changes the material’s inherent transformation stress. Consequently, the heat transfer characteristics of the ambient media play a surprisingly significant role in the macroscopic response of the material (see also Shaw, 2000; Iadicola & Shaw, 2002). This issue is a unique and often counter-intuitive effect. The consequence is that the response time of an SMA as an actuator is governed by thermal scaling laws, in which the effective time constant scales as the volume--to--area ratio of the element. Therefore, large monolithic structures react slowly; whereas, small, thin structures react relatively quickly. For example, better than 30 Hz actuation can be obtained with thin film materials, making this form attractive for many microactuator applications (see Grummon et al., 1999; Grummon & LaGrange, 2000; Ho & Carman, 2000). The reduced volume--to--area ratio of an SMA foam, and the possibility of forced convection of fluids within it, would result in dramatically improved strain--recovery response time compared to monolithic SMAs.

There is experimental evidence (Gall et al., 1999) of significant tension–compression asymmetries in highly drawn or rolled materials due to induced crystallographic texture. Thus, the transformation behavior is dependent on the sign of the hydrostatic component of stress, resulting in different mechanical responses in compression and tension, despite the fact that the transformation dilatation strain is quite small. This tension–compression asymmetry may also exist even in untextured NiTi. There has been some nice work by Sittner et al. (1995) of tension–torsion experiments on SMAs that exhibit complex path–dependence. The mechanics of a sparse SMA foam, which will likely involve bending and twisting modes of slender ligaments at the local scale, will accordingly be complex. Rigorous thermomechanical modeling will likely be quite challenging.

Furthermore, uniaxial stress–induced transformation in NiTi can be accompanied by mechanical instabilities, leading to localization of deformation and temperature and distinct propagating transformation fronts (see, for example, Iadicola & Shaw, 2002). These effects, in turn, lead to extreme rate and environment sensitivities of the constitutive behavior, since transformational activity is confined to the local neighborhood of the transformation fronts. This causes control difficulties when developing uniaxial SMA actuators. In an SMA foam, however, the slenderness of the ligaments will cause them to deform mostly in bending and torsion with large strain gradients across the ligament diameter. These deformation modes should suppress material instabilities that occur under uniform uniaxial deformation. Instead, under crushing, buckling-type instabilities would occur at the cell scale, resulting in localized deformation of the foam. This is precisely the mechanism that leads to efficient energy absorption, and in the case of an SMA foam, the deformation will be recoverable if it occurs by reversible martensitic transformation rather than by slip–mediated plastic yielding.

Another important issue for structural design involving NiTi is its cyclic performance, both from the standpoints of fatigue (reliability) and repeatability (performance). In fact, many suppliers perform cyclic “training” in order to stabilize behavior before delivery to the user. Limits (usually ≈2 % strain) are then recommended by the supplier to address the fatigue concern. Experiments have shown that there is significant transformation softening when virgin NiTi is subjected to constant–strain amplitude cycling (see, for example, Iadicola & Shaw, 2001). The cyclic performance of an SMA foam will likewise need to be addressed, depending on whether the application requires high cycle/small strain service (such as vibration isolation) or low cycle/large strain service (such as energy absorption and armor applications).

Design & Manufacturing Issues of SMA Foams

If the geometry is well–designed the deformation caused by crushing an SMA foam can be recovered by heating or by isothermal removal of load (depending on the ambient temperature). Furthermore, the macroscopic strain recovery capability of an SMA foam can be much larger than the martensite transformation strain, due to the displacement amplification arising from the slenderness of the ligaments and their bending/torsion mode of deformation at the local scale. To achieve a superelastic foam, however, the ratio of the ligament thickness to average cell diameter must be identified such that cell collapse can occur at local strains within the maximum transformation strain inherent in the martensitic transformation. We expect that a sparse foam with a relative density of less than 10% will be needed for this to be successful.

The processing of wrought SMA materials requires tight control of alloy chemistry and careful thermo–mechanical treatments. Several techniques are currently in use for the commercial production of wrought NiTi (Sczerzenie, 1998), including induction skull casting, electron beam cold hearth melting, plasma hearth melting, and direct vacuum arc remelting schemes, but the simplest and most common is vacuum induction melting followed by vacuum arc remelting (VIM/VAR). Subsequent thermomechanical processing during manufacture of the final physical form must then be carefully designed to produce the required microstructure and defect population. Melting, deformation and annealing processes are complicated by several characteristics of NiTi alloys:
NiTi is highly reactive to oxygen, both in the molten state, and in the solid state above a few hundred degrees, requiring processing in an inert environment and/or under a hard vacuum. NiTi also attacks refractory ceramics, although well-cooled graphite crucibles may be used.

The transition temperatures of the resulting material are extremely sensitive to deviation from equiatomic stoichiometry. For example, an extra one percent Ni content can suppress the transition temperatures by as much as 100 °C.

In addition, cold work and annealing treatments have a significant effect on transformation temperatures and the plastic yield strength of the material.

The processing of a SMA foam material presents additional challenges.

• Cold work, as is used in the processing of NiTi in wire or strip form to improve strength, is not practical for most candidate foaming processes. Cold work creates dislocation sites for a favorable dispersion of Ni$_4$Ti$_3$ precipitates, which is often used to improve the subsequent plastic strength. Achieving a fully functional superelastic foam without recourse to such thermomechanical treatments presents a significant challenge.

• Many of the processes used for make Al foams, which involve bubbling of the melt, would be difficult for NiTi foam. Both the density and melting temperature of NiTi (ρ = 6.5 g/cc, $T_m$=1320 °C) are greater than that of Al (ρ = 2.70 g/cc, $T_m$=660 °C). This makes it more likely for drainage to occur before solidification of the foam (see Cox et al., 2001).

Alternative thermomechanical processing must be developed instead to produce desirable properties.

EXPERIMENTAL PROCEDURES AND MATERIALS

For these initial processing experiments we have chosen a powder–metallurgy approach to foam fabrication which has been successfully used to manufacture open–cell structures from a wide variety of alloys (and ceramics), including pure nickel and pure titanium. In this process, a polymeric precursor foam (which determines the ultimate cell size and topology) was first coated with a slurry of NiTi powder in a binder agent. It was subsequently heated to burn out both the polymer foam and binder materials and to finally sinter the remaining powder.

Gas–atomized NiTi powder with composition Ti-50.9Ni (at%) was obtained from Special Metals Corp., New Hartford NY. Analysis of the as–received powder indicated a nominal particle size of -270 mesh with 50% of the particles less than 32 microns in diameter and 10% less than 12 microns in diameter. A series of proprietary binder/solvent systems (Porvair Fuel Cell Technology Corp., Hendersonville NC), designated A, B, C, D, and E, was used to suspend the particles to coat an open–cell polyurethane foam with 3–5 cells per inch. Sintering at several temperatures between 1149 and 1288 °C was carried out in vacuum. Carbon and sulfur levels in the as–fabricated foams were measured using a Leco CS200 analyzer, and oxygen and nitrogen levels were determined on a Leco TC500 instrument. X–ray diffraction measurements were made with Cu-Kα radiation on a Scintag–2000 machine, and differential scanning calorimetry (DSC) was performed on a Perkin–Elmer Pyris 1 system. Scanning electron micrographs were made in secondary electron mode on a Hitachi S-2500 operated at 25 kV using a LaB6 emitter.

EXPERIMENTAL RESULTS

This paper provides a first report on the results of seven separate experimental trials performed at different sintering temperatures and with different binder systems. The outcomes varied widely, both as a function of sintering temperature (with lower temperatures giving incomplete sintering and higher temperatures sometimes resulting in structural collapse), and binder system (which influenced both structural integrity and the level of interstitial contaminant pickup). At the highest temperatures used, sintering could be driven to nominal completion, but the resulting microstructures incorporated significant void porosity. None of the trials gave acceptable results with regard to interstitial contamination, but X–ray diffraction evidence indicated that the cubic B2 phase was present at room temperature. Furthermore, displacive transformation activity could be observed by differential calorimetry, indicating that interstitial contamination may have been superficial. A summary of the process parameters used in the various trials and principal characteristics of the resulting foams are provided in Table 1.

Below we give a brief description of each of the seven sintering trials and discuss selected optical and scanning electron microscopy (SEM) results that show typical examples of the resultant macro- and micro-structures. The small specimen size and irregular shape prevented meaningful measurement of net density, but for most of the materials discussed below the foam density was approximately 5%.

Trial I

Initial experiments using a sintering temperature of 1149 °C resulted in poorly sintered structures. Foams from Trial I, prepared at this temperature using binder system A, exhibited a light brown discoloration and were extremely fragile. Numerous cells were filled with material, and a rough, grainy surface texture indicated a very low degree of particle sintering. Subsequent chemical analysis indicated a significant level of interstitial contamination (C, S, O and N levels were 0.425, 0.003, 0.349 and 0.610 wt%, respectively).
Table 1. Processing Conditions, Composition and Mechanical Characteristics.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Binder</th>
<th>Sintering T (°C)</th>
<th>C (wt%)</th>
<th>S (wt%)</th>
<th>O (wt%)</th>
<th>N (wt%)</th>
<th>Shape</th>
<th>Sinter</th>
<th>Strength</th>
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<tr>
<td>I</td>
<td>A</td>
<td>1149</td>
<td>0.425</td>
<td>0.003</td>
<td>0.349</td>
<td>0.610</td>
<td>Poor</td>
<td>Poor</td>
<td>V</td>
</tr>
<tr>
<td>II</td>
<td>B</td>
<td>1204</td>
<td>0.960</td>
<td>0.002</td>
<td>0.404</td>
<td>0.717</td>
<td>Good</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>III</td>
<td>C</td>
<td>1260</td>
<td>0.910</td>
<td>0.003</td>
<td>0.673</td>
<td>1.231</td>
<td>Best</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>IV</td>
<td>D</td>
<td>1260</td>
<td>0.193</td>
<td>0.002</td>
<td>0.261</td>
<td>0.476</td>
<td>Poor</td>
<td>Poor</td>
<td>V. Poor</td>
</tr>
<tr>
<td>V</td>
<td>B</td>
<td>1288</td>
<td>0.910</td>
<td>0.002</td>
<td>0.947</td>
<td>1.654</td>
<td>Good</td>
<td>Good</td>
<td>Best</td>
</tr>
<tr>
<td>VI</td>
<td>E</td>
<td>1288</td>
<td>0.350</td>
<td>0.002</td>
<td>0.400</td>
<td>0.733</td>
<td>Poor</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>VII</td>
<td>B</td>
<td>1288</td>
<td>0.815</td>
<td>0.003</td>
<td>0.412</td>
<td>0.767</td>
<td>Fair</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>VIII</td>
<td>Loose Powder</td>
<td>1288</td>
<td>0.280</td>
<td>0.002</td>
<td>0.954</td>
<td>1.572</td>
<td>-</td>
<td>Poor</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3. Photograph of foam samples from Trial II.

**Trial II**

For Trial II, the sintering temperature was increased to 1204 °C and binder system B was used. The resulting material was dark neutral gray in color, and although some cells were observed to be filled, the macroscopic structure of this foam (see Figs. 3 and 4) was much improved compared to Trial I, and for the first time a true β-NiTi open–cell foam structure was created. Scanning electron microscopy revealed generally well–formed ligaments and nodes (Fig. 4b), but close inspection indicated that sintering was incomplete (see Fig. 4c). Considerable void porosity was apparent, with voids as large as 40 microns readily observable on the surface of the ligaments (struts) and nodes.

Figure 5 is an SEM image of a strut fractured near a node that illustrates the nominally triangular cross–section of the ligaments, and it clearly shows the large central void left behind by the fugitive polyurethane support structure. Although the grainy surface texture again indicates poor sintering, the figure shows a regular tetragonal scaffolding structure with distinct slender struts. The topology and the triangular cross–section of each strut arises from the polyurethane precursor foam geometry. In addition, each ligament is hollow where the precursor foam burned away. For applications requiring crushing and recovery of the SMA foam, we consider this geometry of nodes and slender, hollow ligaments to be a significant improvement over the ran-

Figure 4. Close–up images of foam sample from Trial II: (a) photograph, (b) SEM image showing ligaments, (c) SEM image of ligament showing incomplete sintering.
dom void structures seen in previous porous SMAs. This also demonstrates that the foam structure can be tailored to the ultimate application through the judicious choice of precursor foam structure.

Although it was much stronger than the product of Trial I, the mechanical properties of this material were still rather poor and the foam was weak and extremely brittle. Interstitial contamination levels (0.96, 0.002, 0.404 and 0.717 wt% for C, S, O and N, respectively) were elevated over those of Trial I, presumably as a result of the higher sintering temperature. (Apparent sources of these contaminants are discussed further below.)

**Trial III**

For the third trial, binder system C was used, and the sintering temperature was further increased to 1260 °C (within 50 °C of the nominal melting point of the alloy\(^1\)). The open cell foam structure is well-defined as can be seen in the optical photograph in Fig. 6. The density was estimated at 3.9%, the least dense of all the trials. Although the material was brittle, its mechanical strength was qualitatively better than for Trials I and II. As is apparent in Fig. 7, however, the powder was still incompletely sintered. Interstitial C, S, O and N levels (0.91, 0.003, 0.673 and 1.231 wt%, respectively) were again elevated at the increased sintering temperature.

**Trial IV**

A foam also sintered at 1260 °C, but instead using binder system D, showed a significant drop in interstitial contamination levels (C, S, O and N contents were 0.193, 0.002, 0.261 and 0.476 wt%, respectively). However, in this case the structure partially collapsed during burnout and/or sintering, apparently due to the failure of the binder.

**Trial V**

In Trial V, a two-step slurry-dip and sinter was used. The foam was prepared using binder system B and was first sintered at 1204 °C using the same methods employed in Trial II. The sintered structure was then recoated with a slurry made with binder B, and sintered a second time at a higher temperature of 1288 °C (within 15 °C of the nominal solidus temperature). In fact, this sintering temperature may have actually been above the

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\(^1\)TiNi melts congruently at 1310 °C for a composition that is nominally 50.5 at% Ni. Based on the slope of the phase diagram solidus, the melting temperature for the 50.9 at% powder used in this study is estimated at 1303 °C.
solidus for at least some of the particles in the distribution, since the foam structure sagged and pooled locally during the second sintering cycle. The density was estimated at 15%, the most dense of all the trials. The surviving foam regions did, however, exhibit qualitatively high strength, and the foam could not be crushed using hand tools. Machining marks left on the surface after mechanical grinding (see Fig. 8) were suggestive of at least some room-temperature ductility. SEM examination revealed nominally complete sintering, as seen in Fig. 9, but the structure contained large numbers of voids, many as large as 20–30 microns in diameter. Contamination was severe with C, S, O and N contents 0.91, 0.003, 0.673 and 1.231 wt%, respectively.

For gas-atomized powders, such as those used in the present study, composition may be a weak function of particle size. The volatility of titanium causes it to be depleted more severely in the smallest particles. The resulting nickel enrichment lowers the solidus temperature by about 270 K per at% increase in Ni.

Discussion

The foams described above all suffered severe carbon, oxygen and nitrogen contamination with the worst case showing more than 3.5 wt%. These levels must be reduced by a factor of 50 before good shape-memory and superelasticity characteristics can realistically be obtained. Contamination levels depended

Trial VI

A second foam was sintered at 1288 °C used a single slurry process, but this time with binder system E. This foam collapsed severely during sintering. Interstitial contents were more moderate than for the two-step foam from Trial V (C, S, O and N were 0.35, 0.002, 0.400 and 0.733 wt%, respectively).

Trial VII

In yet another experiment, a foam was prepared using binder system B and also sintered at 1288 °C, producing a foam that was partially collapsed. The end product of Trial VII was, however, reasonably well-formed as can be seen in the images in Fig. 10a, and the foam had qualitatively good strength. SEM examination indicated nominally complete sintering (see Fig. 10b), but considerable void porosity was evident as can be seen in Fig. 10c. C, S, O and N contents were similar to those of Trial VI (0.815, 0.002, 0.412 and 0.767 wt%, respectively).

Figure 10. Close-up images of foam sample from Trial VII: (a) photograph, (b) SEM image showing improved sintering, (c) SEM image showing porosity of ligament.
strongly on binder selection, and also tended to increase with increasing sintering temperature, as can be seen in Fig. 11.

Also shown on this plot are data from an additional experiment that was conducted to assess the amount of interstitial contamination attributed to the burnout of the polyfoam skeleton and binder, as opposed to pickup of gaseous contaminants from the ambient vacuum. For this purpose a thin layer of loose powder was sintered at 1288 °C in the same run as Trial VII. Levels of C, S, O and N found in the sintered product were 0.280, 0.002, 0.954 and 1.572 wt%, respectively (indicated as ‘LP’ in Fig. 11). When these data are compared to the best results obtained for foams in the present study (observed in Trial IV for binder system D), the results indicate that substantial carbon pickup (0.6 wt%) can be attributed to binder burnout for binder systems B and C, but that in the case of binders D and E carbon pickup may be associated simply with vacuum contaminants. In all cases, oxygen, nitrogen and sulfur pickup is also largely attributable to vacuum system contaminants, since the levels in the sintered loose powder were similar to or greater than those observed for most of the foam trials. It is therefore quite possible that interstitial solute contamination can be eliminated through the use of more rigorous vacuum practice.

Notwithstanding the excessive contamination levels in these foams, evidence of both a B2 parent phase structure and martensitic transformation were experimentally demonstrated. X–Ray diffraction spectra from the foam made in Trial VII, shown in Fig. 12, displays a prominent peak at 42°–43° (2θ, Cu-Kα) indicating the presence of β-NiTi with the cubic B2 austenite crystal structure. Counts rates were moderate for this low–density foam structure, and additional peaks were present that are probably associated with various oxides, carbidies or nitrides of titanium. But more importantly, differential scanning calorimetry (DSC) data showed unambiguous martensitic transformational behavior, as seen in Fig. 13, which compares the as–received powder with a foam sample from Trial II. The foam material shows martensite peak (M_p) temperatures that are 10 to 15 °C lower than for the raw powder, and austenite peak temperatures (A_p) that are ≈ 30 °C lower than the corresponding temperatures for the as–received powder. Transformational enthalpies are also noticeably diminished, but the presence of the DSC signals may indicate that normal martensitic transformation took place in the interior of the structures (away from exposed surfaces) and was suppressed only in a heavily contaminated surface layer. In other words, severe interstitial contamination may only be a superficial phenomenon and thus amenable to chemical removal.
SUMMARY AND CONCLUSIONS

Experiments using a precursor, sacrificial foam and a powder–metallurgy approach have shown that a low density open–cell NiTi foam can be fabricated. The presented technique is attractive, since the topology of the foam can be tailored through the choice of precursor foam. Furthermore, a lower foam density (5% dense) is possible than previous hot isostatic pressing (HIP) or combustion synthesis (CS) techniques (near 50% dense). X–ray diffraction experiments show that the material has the desired ordered intermetallic (B2) structure. The material also displays the calorimetric signature of martensitic transformational behavior. Problems associated with interstitial contaminant pickup must be solved before good superelastic properties can be achieved. Fortunately, contamination may be limited to chemically etchable surface zones and more rigorous vacuum technique and prudent binder choice may alleviate the contamination problem altogether.

Experiments are in progress to determine proper powder composition, size distribution, and physical form (atomized vs. machined powder stocks), and to develop optimized processing procedures, temperatures and binder chemistries. Clearly, more rigorous vacuum practice will be needed, and novel variations on the current powder–metallurgical practice may be required. However, if functional NiTi shape–memory and superelastic foams can be successfully produced it is also likely that ternary Ti(NiCu), (TiHf)Ni, TiNbNi and Ti(NiPd) variants will also be practical, allowing adjustment of strength, transformation temperature and hysteresis over broad ranges.

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