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RESEARCH

Lightweight and Highly Porous Ni-Ti Alloy Foams Synthesized by Powder Metallurgy using NaCl as Space Holder

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ABSTRACT

Lightweight Ni-Ti alloy foam has received immense attention as a promising material for sensors, actuators, dampers, biomedical implants, and energy absorption applications due to their outstanding properties including low density, high surface area, corrosion resistance and excellent mechanical strength. In the present study, we developed Ni (50)-Ti (50) alloy foams with varying porosities using NaCl as a space holder. The cold compacted mixture of NiTi alloy powder, NaCl granules, and 2 wt% polyvinyl alcohol (PVA) solutions are mixed uniformly in a globe box for 8 hrs. Sintering is carried out in two stages: firstly, at 900 ºC for 2 hrs and then at 1100 ºC for two hrs. During sintering, NaCl gets melted and removed from the foams. The Ni-Ti alloy foams exhibit an excellent compressive strength of 48 MPa at a relative density (ρ_{rd}) of 0.45. It also provides higher plateau stress, greater strain hardening effect, and larger strain recovery. Thus, the lightweight high strength Ni-Ti alloy foam is a promising material for bone implants and energy absorption applications.

KEYWORDS

Metals and alloys; porous materials; Ni-Ti foam; space holder; plateau stress

INTRODUCTION

NiTi (Nitinol) foam has outstanding properties such as high strength, good ductility, shape memory effect, and better corrosion resistance [**1,2**]. Due to their outstanding properties, these Ni-Ti alloys foam can be used for multifunctional applications such as high damping and high energy absorption [**3**], sensors and actuators [**4**], and bio-implants [**5,6**]. In the case of bio-implants, these materials are preferred only because of good bio-inertness and low stiffness as compared to Ti and other metals or alloys. The shape recovery effect with temperature makes them an ideal candidate for actuators and sensors [**4**]. The porosity of Ni-Ti foam can affect the bio-compatibility as well as shape recovery rate [**7**] because the stress, modulus, and heat transfer vary with the porosity fraction. The strength and modulus of the bone can be tuned by changing the porosity of the foam [**8**]. The bone construction and heat transfer can be controlled by controlling the pore size and cell size of the foam. Because of the above-mentioned properties, large attention has been paid to making Ni-Ti foams and characterizing them in terms of foam fabrication and mechanical properties. For the development of metal foam, different types of space holder materials have been used. However, for the synthesis of Ni-Ti foams, generally, NaF and NaCl have been used as space holders [**8,9**]. NaF and NaCl were chosen because of their high melting point which allows Ni-Ti powder-NaF/NaCl powder mix to be hot compacted at high temperatures where partial sintering would take place. In most of the above cases, mainly the samples after cold or hot compaction are sintered at relatively low temperatures and then NaCl is leached out from the sintered samples. After leaching out of NaCl or NaF, the samples again sintered at high temperatures. Thus, the sintering is done in two and three stages. The time and cost can be reduced if the sintering stage is reduced and NaCl is removed through partial melting during sintering. Furthermore, this is attributed to the fact that Ni-Ti foam is much more difficult to process in the liquid state, due to its very high melting point (1310ºC) and its extreme chemical affinity with atmospheric gases (i.e. oxygen and nitrogen) above 400ºC. Also, it is very difficult to control the porosity and cell size of Ni-Ti foam by liquid metallurgy route. Therefore, we have adopted the simple and cost-effective powder metallurgy route in which NaCl was used space holder. By the space holder method, the foam with the desired porosity and cell size can be made. In the present investigation, the NI-Ti foams with high porosities have been developed using NaCl as a space holder and investigated for structural morphological and mechanical properties.

EXPERIMENTAL

Ni(50)-Ti(50) shape memory alloy (SMA) foams with varying porosities (ranging from 55 to 85%) were made using NaCl as a space holder through powder compaction and sintering technique. The size of the pore is also controlled by controlling the size of NaCl. The cold compacted mixture of NiTi alloy powder, NaCl granules, and 2 wt% polyvinyl alcohol (PVA) solution is mixed uniformly in a globe box for 8 hrs. For the fabrication of Ni-Ti Foam with varying porosities (50-80%), the amount of Ni-TI and NaCl was calculated by the following equation;

$$\frac{W_{Ni-Ti}}{W_{NaCl}} = \frac{\rho_{Ni-Ti}\,(1-V_{NaCl})}{(\rho_{NaCl} \times V_{NaCl})} \tag{1}$$

where, $W_{Ni\text{-}Ti}$ and W_{NaCl} are the weight of Ni-Ti and NaCl powder respectively, whereas $\rho_{Ni\text{-}Ti}$ and ρ_{NaCl} are the density of Ni-Ti and NaCl powder respectively. After that mixed powder was molded into a cylindrical shape of the size 20 mm diameter and 25 ± 0.5 mm height using a hydraulic press at a pressure of 300 MPa. Sintering is carried out in a two-step sintering process firstly sintering was done at 900ºC for 2 hrs and then at 1100ºC for 2 hrs at a vacuum level of 10^{-4} mbar. During sintering, NaCl gets melted and the maximum amount of NaCl is removed from the Ni-Ti foam samples. Further, to remove the remaining amount of NaCl from the Ni-Ti foam samples, the sintered foam samples were heated in a hot water bath at 100ºC for 24 hrs. During this process, the NaCl dissolved in water and was removed from the samples. The sample weights were measured every 6 hrs of heating to ensure the removal of salt from the foam samples. It was found that after 24 hrs, salt got removed from the foams totally, as no further weight loss was noted. The schematic diagram for the fabrication of Ni-Ti foam is shown in **Fig. 1**. The foams are characterized in terms of cell size, relative density, compressive deformation behavior, and strain recovery. XRD and EDX analysis of foam samples after sintering is carried out. The density of foam samples was measured for determining the fraction of porosities. The pore size was measured from the SEM micrographs of foam samples. The compressive deformation of sintered foam samples was carried out at a strain rate of $10^{-2}\,s^{-1}$. The pseudo-elastic strain of these foams was carried out from loading-unloading curves during compaction loading. The plateau stress and densification strain of the foam samples were measured from the stress-strain diagram of these foams.

Characterizations

To examine the morphology and elemental composition (EDS) of NI-Ti Foam the scanning electron microscope (SEM, JEOL: model: 5600) was used. X-ray diffraction (XRD, Bruker D8 Advance) with a Cu K radiation source (=0.15406 nm) at 40 kV was used to evaluate the crystal structure of Ni-Ti foam in the range from 30 to 80 degrees. Universal testing equipment (Instron 8801), was used to measure the compressive stress-strain curve of Ni-Ti foams.

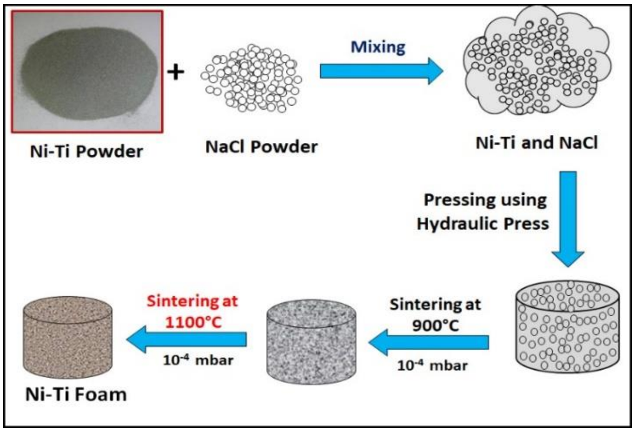

Fig. 1. The schematic diagram for the fabrication of Ni-Ti foam

RESULTS AND DISCUSSION

The Ni-Ti foams were made from pre-alloyed powder with an average size of 20±2 μm. The average size of the NaCl space holder was 350±2 μm. To get the desired amount of porosity, the measured quantity of alloy powder and NaCl particles are mixed. As the sintered samples are characterized firstly in terms of porosity vis-à-vis relative density. The volume fractions of porosity as a function of NaCl content and sintering schedule are shown in **Table 1**. It was observed that the sintered samples exhibit around reasonably higher porosity than the volume fraction of NaCl. The difference is quite less at a higher volume fraction of NaCl. The microstructures of the sintered samples with varying porosities are shown in **Figs. 2(a-c)**. It is noted that the average cell size is around 350 ±2 μm and the cells are connected with a tiny opening in the cell wall between the neighboring cells. **Fig. 2(d)** showed that there are micro porosities in the cell wall or cell edges which also allow for fluid flow and the extent of porosities in the cell wall is around 10 to 15%. Because of this fact, the measured porosities are much higher than the expected porosities. At a higher volume fraction, for example, at 80% NaCl space holder, only 20 % Ni-Ti powder is there which is forming the cell wall and edges. If the cell wall contains around 15% porosities, the maximum level of difference would be only 3%. This porosity is coming because of solid-state sintering. **Fig. 2(e)** shows the High-resolution image of Ni-Ti foam with RD of 0.22. This is again due to particle deformation during hot compaction which reduced the interparticle porosities in the cell wall. The elements present in the NI-Ti foam were analyzed by EDX and shown in **Fig. 2(f)**. It was found that the large contents are Ni and Ti and some small content of carbon due to residual PVA was also observed. No other residual of NaCl particles was observed. The XRD pattern of sintered Ni-Ti alloy foam showed NiTi and $NiTi_3$ phases (**Fig. 3(a)**) [**10**].

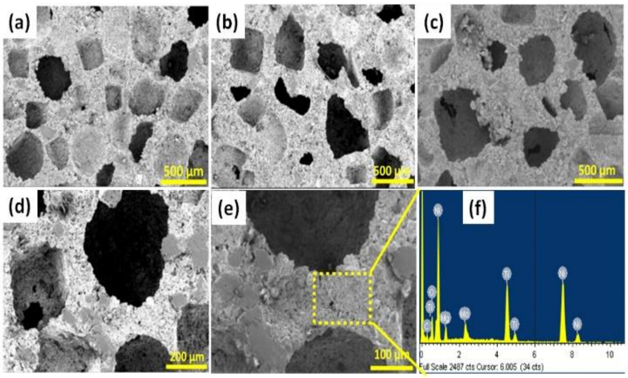

Fig. 2. Microstructures of Ni-Ti foam using NaCl as space holder: (a) RD = 0.42, (b) RD = 0.33 (c) RD= 0.22, (d) micro porosities in the cell wall and inter-cell boundaries (RD=0.22), (e) High-resolution image showing strongly bonded cell wall and (f) EDX analysis of Ni-Ti foam.

Table. 1. Variation of plateau stress, densification strain, and pseudo-elastic strain recovery as a function of relative density.

R.D.	Porosity (%)	Plateau Stress (MPa)	Densification Strain	Strain recovery (After 8% strain)
0.45	55	48	0.32	4.1
0.32	68	30	0.42	4.0
0.22	78	12	0.44	3.6
0.15	85	5.0	0.65	3.2

The Compressive stress-strain curves are shown in **Fig. 3(b)**. The curves showed hardening behavior in the plateau region unlike most of the foam samples. The elastic strains are noted after 8 %. The curves further state that the extent of strain hardening is more prominent at higher relative density. This is because of the greater extent of Ni-Ti present in those samples. The hardening may be due to phase transformation during deformation. A set of samples are deformed up to different strain levels and then the load is released at room temperature. The tests were conducted at a strain rate of 0.01 s^{-1}. The recovery strain is then determined to form these loading-unloading curves. It was noted that elastic strain recovery ranges from 3 to 4.1%. The elastic strain recovery is a function of relative density. At higher relative density, elastic strain recovery is marginally higher (**Table 1**). This is also due to less porosity and a greater extent of Ni-Ti in the foam samples. A detailed study of its SMA effect and its utility for bio-implants and other applications is to be explored.

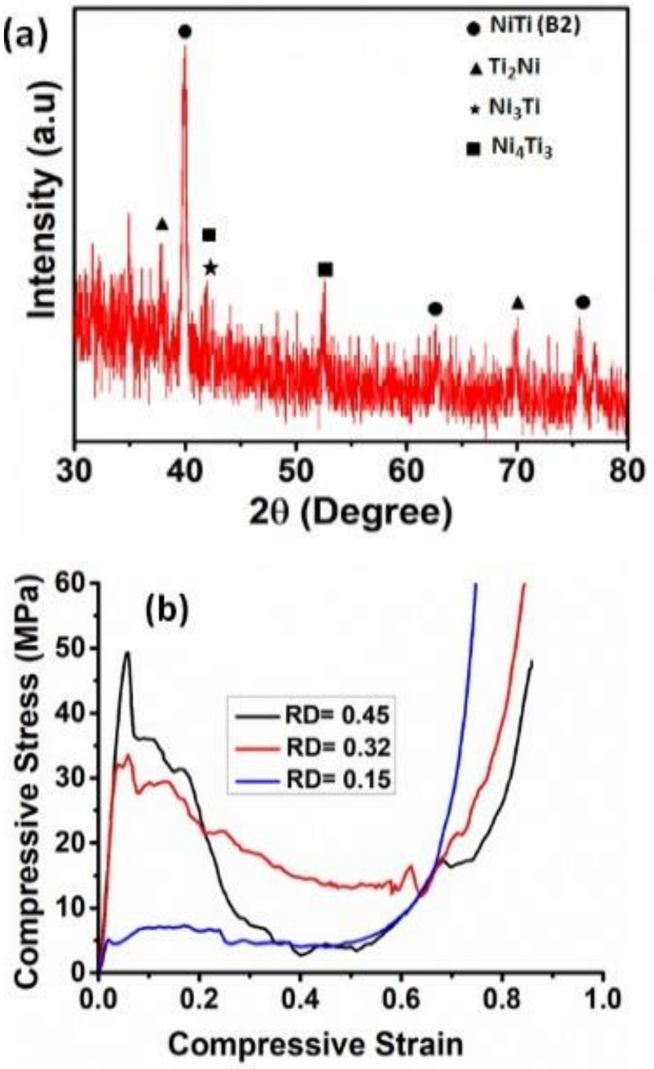

Fig. 3. (a) XRD pattern of Ni-Ti foam and (b) Compressive strength of Ni-Ti foam with varying relative densities.

CONCLUSION

Ni-Ti pre-alloyed powder can successfully be utilized for making Ni-Ti foam following the space holder technique. NaCl will be an excellent space holder. The foam can be made using a single-stage sintering process. The porosity, size, and shape of the foam can be controlled by controlling the volume fraction and shape and size of NaCl. The porosity is noted to be close to the expected porosity when the foam is made through hot compaction and sintering. It also provides higher plateau stress, greater strain hardening effect, and larger strain recovery. The cell wall contains porosities that allow fluid to flow through it. In the future, these novel and lightweight Ni-Ti foams are believed to be used in many applications, ranging from the bone implant, and spinal fixation to acetabular hip prostheses, dental implants, permanent osteosynthesis plates, sensors, actuators, aerospace components, etc.

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CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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