Journal of Metals, Materials and Minerals, Vol.22 No.1 pp. 39 - 44 , 2012

Porous NiTi Produced by NiTiTa Transient-Liquid-Assisted Method

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Abstract

This work presents a novel method for preparing porous NiTi by powder metallurgy using a vacuum sintering technique. Tantalum was used as a transient liquid phase creator, which enhanced the sinterability of NiTi powders. The effect of Ta content and powder packing on the degree of densification were investigated. The porous NiTi exhibited shape memory behavior and a large recovery strain, analyzed by differential scanning calorimetry and compressive testing, respectively, making the material promising for bone implant applications. In addition, macroporosity was created by using NaCl spaceholders. Adding 3 atomic percent of Ta and 60 volume percent NaCl space-holder resulted in a foam containing 60 percent porosity with an average pore size larger than 100 micrometers. A new type of metallic spaceholder, coarse Ta powder, was also demonstrated here, and functioned simultaneously as a densification enhancer and space-holder.

Keywords : Metal foam, Nickel-titanium alloy, Tantalum, NiTi-Ta, Sodium chloride

Introduction

Various powder metallurgical methods for producing porous nickel titanium (NiTi) have been established in the past decade. Almost all share the same goal of producing a highly interconnecting porous structure, with 30-80% porosity and pore size larger than 50 μm, that is strong (>100 MPa) but low stiffness (<20 GPa). These features are required of a suitable load bearing framework for bone implant applications, one of the major applications for which porous NiTi has been proposed.

Due to slow diffusion in the NiTi system, many researchers have used exothermic reactions between premixed Ni and Ti powders to deliver such structures, while a few others used pressure-assisted methods (i.e. hot isostatic pressuring and hot pressing) on prealloyed NiTi powders.[(1)] The latter approach provided better control of NiTi composition, which resulted in a reliable shape recovery response (i.e. shape memory effect or superelastic effect), but required prolonged sintering times (where vacuum sintering was also usually applied), or costly high-pressure setups.

Transient liquid-phase sintering is a promising solution to allow faster sintering of prealloyed NiTi in a simple vacuum sintering furnace, lowering cost and production time. A melting point depressant used for NiTi system is required not only to initiate the transient liquid, but also to ensure that the solidified liquid phase is biocompatible and maintains the shape recovery properties of NiTi. Based on these criteria, tantalum and niobium, which have very similar characteristics, are both more appropriate candidates than copper or iron. Tantalum in pure form is very

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biocompatible and provides excellent visibility in x-ray images; indeed it has been competitive with porous NiTi for prosthetics. Its addition to NiTi can improve corrosion resistance, increase ductility, and yield a shape memory effect with broader hysteresis.[2,3] In addition, tantalum is well known for the use of liquid phase as an interlayer phase to weld NiTi to other metals (e.g., steel).[4] Spaceholders have been successfully used to enable direct control of pore characteristics such as pore size, shape, and porosity. Common spaceholder materials are salt (e.g., NaCl, NaF), polymers (e.g., PMMA), and other organics (e.g., NH_4HCO_3, urea).[5] The presence of spaceholders within the bed of NiTi powders can modify the overall powder packing, and thus affect densification upon sintering, usually resulting in large amounts of microporosity in the metal struts. Therefore, using transient liquid phase sintering with the spaceholder method to create a controlled macroporosity while avoiding microporosity in struts is quite a challenge. The present work explores the possibility of using the NiTiTa transient-liquid assisted method to produce porous NiTi. The porous structure and properties of the porous NiTi were studied using microscopy, differential scanning calorimetry (DSC), and compression testing. The effect of spaceholders such as NaCl and coarse tantalum powder on the porous structure are also discussed.

Materials and Experimental Procedures

Preparation of Porous NiTi samples

Prealloyed NiTi powders(48.6 at.%Ni, 44-177 μm size), from Specialy Metals (USA) and tantalum powders (99% purity, 10 μm mediun size), from H.C.Starck (Thailand) were mixed with NiTi:Ta atomic ratio 97:3 at a speed of 50 rpm for 2 hours. The powder mixture was pressed uniaxially to 40 MPa in a platen press (Gotech GT-7014) in a 12.7-mm-diameter die into a 1 cm^3 pellet. The pellet was then subjected to sintering in a vacuum furnace (Schmetz-I45/1H, Powder Metallurgy Laboratory, MTEC) for 10 hours at 1190^{o}C, which is the eutectic temperature of binary NiTi-Ta.[3] A sample made from NiTi powders without tantalum was pressed and prepared in the same conditions as a control sample. Other samples prepared with different NiTi:Ta ratios and sintering times are listed in Table 1. To investigate the effect of spaceholders, rectangular NaCl powders (laboratory grade, 100-300 μm in size) were added with a metal (NiTiTa) to NaCl volume ratio of 4:6, and further mixed for 2 hours. In the case of tantalum spaceholders, spherical coarse tantalum powders (median size 80 μm, provided by H.C.Starck) were mixed with a NiTi:Ta atomic ratio 97:3 and pressed with the same procedure used for the first sample.

Characterization

Pore structure was observed via optical microscopy (Nikon Eclipse ME600) and scanning electron microscopy (Philips XL30). The sample was cut parallel to the axis of pressing to reveal the vertical cross section using an diamond saw (Imptec PC10), then polished with 320 μm SiC paper and finished with 1 μm alumina suspension. Pore size and porosity were determined by the line-intercept method. To study phase transformation behavior, ca. 10 mg of material was cut and evaluated by DSC in an aluminium crucible (Mettler Toledo DSC822, MTEC), cycling twice from -60 to 150^{o}C at a heating/cooling rate of 10^{o}C/min. The second DSC cycle was used to determine transformation temperatures and heat of transformation. For compression testing, a 4x4x8 mm^3 specimen was cut and subjected to compression using a 25kN load cell at a constant displacement rate of 0.05 mm/min. The specimen was compressed in a universal testing machine (Hounsfield model H50KS) to a strain of 7% before heating in a furnace to 180^{o}C to evaluate the recovery strain caused by the shape memory effect.

Table 1: Sample preparation conditions.

Sample	NiTi:Ta (at.%)	Metal: NaCl (vol.%)	Sintering time (hr.)
NiTi-10H	100:0	0	10
NiTi-3Ta-10H	97:3	0	10
NiTi-3Ta	97:3	0	5
NiTi-2Ta	98:2	0	5
NiTi-1Ta-NaCl	99:1	60	5
NiTi-3Ta-NaCl	97:3	60	5
NiTi-5Ta-NaCl	95:5	60	5
NiTi-3CTa-10H	97:3	0	10

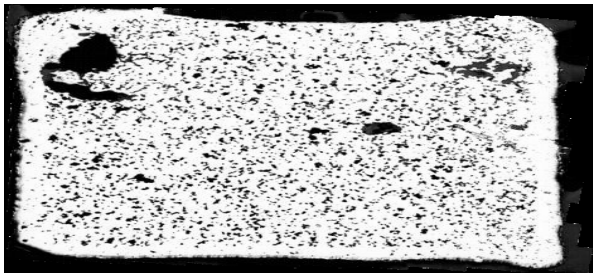
Results and Discussion

Study of Tantalum as a Densification Enhancer in Porous NiTi

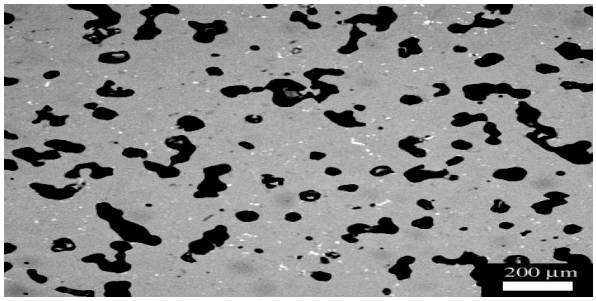
Effect of Ta Addition

The cross sections of sample NiTi-3Ta-10H in Figures 1a and 1b show the first porous structure produced by the NiTiTa transient liquid-assisted method. Total porosity was ca. 15 vol.%, consisting mostly of pores averaging 100 µm in size, with large pores >400 µm in size in some regions, presumably where low initial powder packing occured. When compared to the Ta-free control sample (NiTi-10H, Figure 1c), interparticle micropores were noticeably absent, and pores were rounded in shape and uniformly distributed across the sample.

Similarly dramatic changes in pore structure were observed in previous work in the NiTiNb system.[6] Tantalum, like Nb, acts as a melting point depressant and creates a eutectic liquid phase that helps consolidate the structure during sintering; but more porosity remained here compared to earlier work (15 vol.% vs 6 vol.%) due to the lower compacting pressure used (350 MPa vs 40 MPa).



(a)



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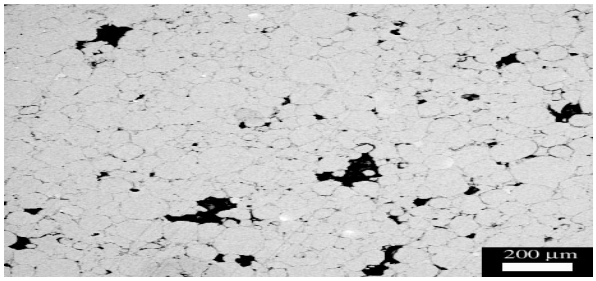


(c)

Figure 1 : Cross - sectional micrographs showing the pore structure of NiTi-3 Ta-10 H at low (a) and high (b) magnifications, compared with that of a Ta -free control sample NiTi-10 H (c) .

Sample NiTi - 3Ta - 10H showed compressive strengths Figure 2 of 380 MPa at strain of 7%. During unloading from 7% strain, the sample showed a 2.5% unloading strain followed by 73% shape recovery of the residual strain (3.5%) through heating to 180°C.

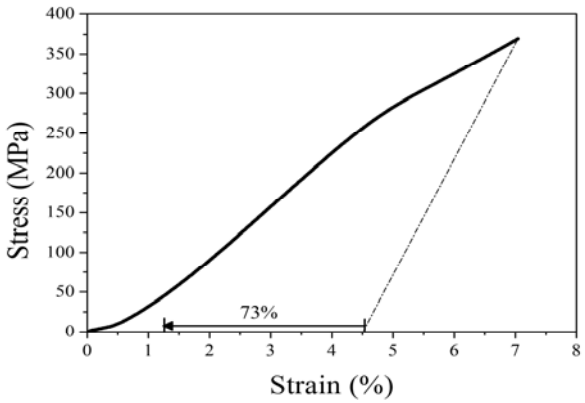
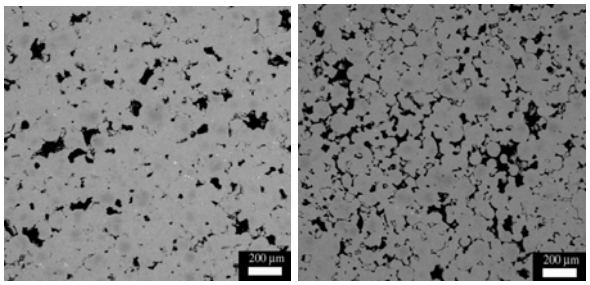


Figure 2: Compression stress-strain curve of sample NiTi - 3Ta - 10H to 7% strains. The arrow along the x-axis represents shape recovery effect during heating at 180°C.

Effect of Sintering Time and NiTi:Ta Ratio

As shown in Fig 3a, decreasing the sintering time from 10 hours to 5 hours resulted in slightly higher porosity (20%) with similar pore size range, and a slight but noticeable increase in the wall microporosity relative to the sample shown above. Figure 3b shows that decreasing the Ta concentration from 3 at.% to 2 at.% created necks and narrow gaps between individual NiTi powders, suggesting that insufficient liquid phase was created to close the micropores. Although high porosity is the aim of this work and both these adjustments led to higher porosity, the preferred pore size is larger, the preferred pore shape is more rounded, and generally the pore characteristics need to be more controlled than was obtained in these two cases. Therefore, the samples in Figure 3 are taken as evidence that sintering times of 5-10 hours and Ta concentrations of 3 at.% are already close to the minimum requirements for creating a viable pore structure.



(a) (b)

Figure 3: SEM micrographs of (a) sample NiTi-3Ta and (b) sample NiTi-2Ta.

Effect of Spaceholders on Pore Structures Produced by Transient Liquid Phase Sintering

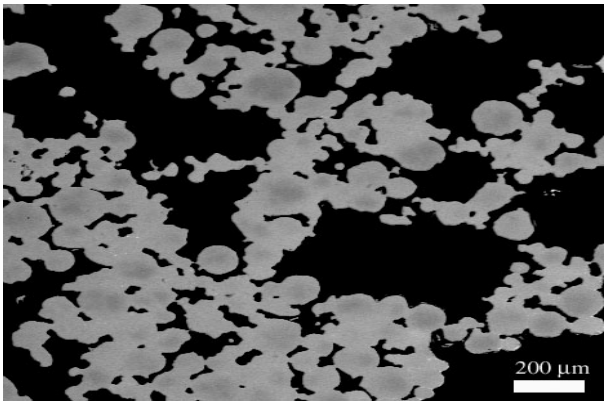
Blocky NaCl Powders as Spaceholders

Adding NaCl to the 3 at.% Ta mixture (Figure 4a) produced a porous structure with 60% porosity, consisting of 40% macroporosity (>100 µm in size) created by blocky NaCl spaceholders and the remaining 20% porosity appearing within the NiTi struts. This high NiTi wall porosity is believed to result from interruption in packing caused by the presence of the NaCl. Most macropores were rectangular in shape and seem to replicate the NaCl shape, while others were irregular, likely due to agglomeration of NaCl powders or pore collapse during sintering. When the amount of tantalum was increased to 5 at.% in an effort to close the wall porosity (sample NiTi-5Ta-NaCl, Figure 4b), the higher liquid volume produced seemed to weaken the macropores, causing more to collapse and making the pore structure more irregular, rather than densifying the wall micropores. Conversely, when only 1 at.% Ta is used (sample NiTi-1Ta-NaCl), smaller necks between powders were observed.

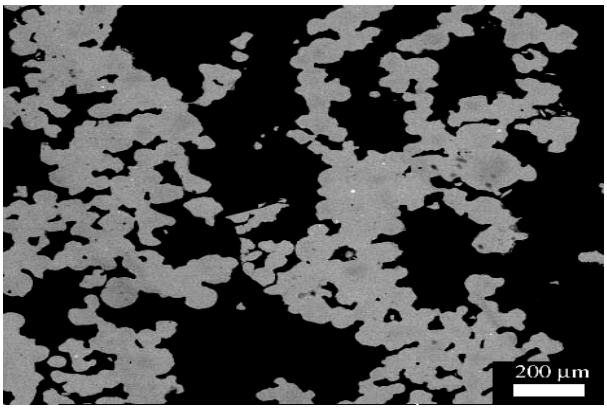
Although the proper ratio of NiTi to tantalum seems to be 97:3 at.% in both the non-spaceholder and spaceholder experiments, the efficiency of this method seems to depend rather strongly on packing of

the base powders in which the liquid phase is created. For instance, the low compacting pressure used here (40 MPa), coupled with the disruptive presence of NaCl, may have created insufficient capillary force between NiTi powders to help the *in situ* liquid wick through the structure.

As shown in Figure 5, transformation temperatures were shifted upwards (by about 50^{o} C), and presented a broader range than those of the starting NiTi powders and the control sample, while the heat of transformation decreased (especially in the sample without spaceholders). Adjusting the amount of tantalum (1-5 at.%) or the presence or NaCl did not give any significant effect on the transformation behavior of the porous NiTi. The cause of this change in transformation behavior is under investigation.



(a)



(b)

Figure 4: Micrographs of samples (a) NiTi-3Ta-NaCl and (b) NiTi-5Ta-NaCl.

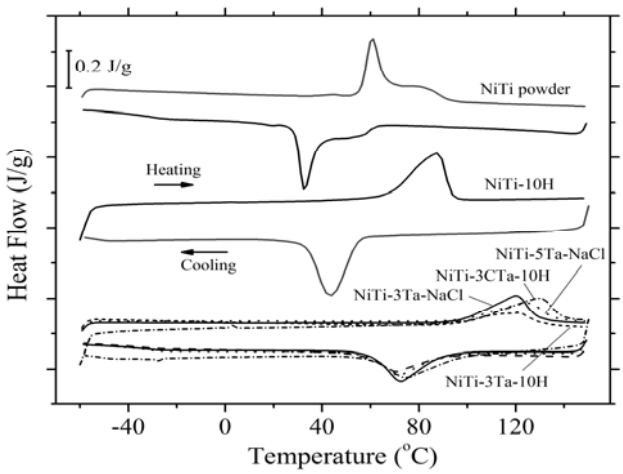


Figure 5 : DSC traces comparing transformation behavior for prealloyed NiTi powders and various porous NiTiTa samples.

Spherical Coarse Ta Powders as Spaceholders

To improve the packing density of the NiTi powders as well as create desirable macropores, spherical coarse Ta powders were chosen to serve as both spaceholders and densification enhancers. As seen in Figure 6 (sample NiTi-3CTa-10H), large round pores (>200 µm) were indeed obtained at the sites which coarse tantalum powders formerly occupied. As in the NaCl case, some pores were irregular due to the replication of agglomerated spaceholders. Within the NiTi walls, a few small pores (ca. 30 µm) were retained from the green porosity, but a significant amount of this microporosity was eliminated. Using the same tantalum concentration and sintering conditions as the earlier sample NiTi-3Ta-10H, therefore, this sample NiTi-3CTa-10H achieved higher porosity with larger pore size, without the apparent drawbacks of NaCl. Moreover, DSC results showed the same effect of Ta addition on transformation temperature. Use of Ta as a simultaneous spaceholder and densification enhancer is therefore a promising alternative processing route for porous NiTi. Further investigation on processing variables such as the volume fraction of coarse tantalum

powders and packing density is already in progress.

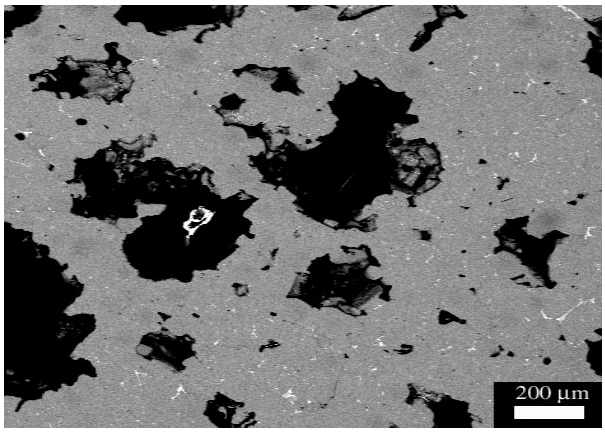


Figure 6 : Micrographs of sample NiTi-3 CTa-10H.

Conclusion

Tantalum powders were used to create transient-liquid phase sintering of NiTi powders in order to produce porous NiTi. Two processing approaches were demonstrated: (1) small tantalum powders acted as densification enhancers and NaCl as spaceholders, and (2) coarse tantalum powders acted simultaneously as densification enhancers and spaceholders. Variables such as packing density, NiTi to Ta ratio, and sintering time show significant effects on the resulting porous structure. Porous NiTi produced by these novel methods exhibits phase transformation while porous structure can potentially be controlled for use in bone implant applications.

Acknowledgments

This research was supported by National Metal and Materials Technology Center (Thailand), grant number MT-B-53-BMD-11-184-G. The author also gratefully acknowledges; support from Center of Advanced Studies in Industrial Technology, Faculty of Engineering, Kasetsart University, and technical advice from Dr. Alan H. Brothers.

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