An Investigation of the Synthesis of Ti-50 At. Pct Ni Alloys through Combustion Synthesis and Conventional Powder Sintering

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Porous Ni-Ti shape memory alloys (SMAs) have been successfully fabricated by the conventional powder sintering and combustion synthesis. In the present study, the microstructure, phase transformation, mechanical property, and stress-strain behavior of porous Ni-Ti SMAs have been investigated.

I. INTRODUCTION

Normally, metals and alloys are used as surgical implants for artificial bones. The biomaterials industry worldwide has an annual turnover of $2.3 billion in the field of hard tissue repair and replacement (total of $12 billion), and there is an increasing growth rate of 7～12% per annum for biomaterials in clinical applications. However, various problems related to common metallic implants occur due to the mismatch between the implants and the replaced bones. For example, the mechanical deformation behavior of bone, which has a high recoverable strain (≥2%, Figure 1), is very different from that of common metallic materials and only the pseudoelasticity (PE) of shape memory alloys (SMAs) is similar in this way;[1] moreover, the yield stress and Young's modulus of bulk Ni-Ti and some other bulk biomaterials are very high and difficult to adjust by subsequent heat treatment, while by controlling the synthesis conditions it is easy to adjust the mechanical properties, such as the strength and Young's modulus, of porous Ni-Ti SMAs to match those of replaced bones. Thus, porous Ni-Ti SMA has recently been acknowledged as one promising biomaterial for bone repair because of its excellent mechanical property, good corrosion resistance, high biocompatibility, and special PE and shape memory effect.[2] Moreover, its low density makes the implant portable and the process simple, and its porous structure not only gives to body tissue the possibility to grow inside and thus providing a reliable anchorage for implant-to-bone but alos allows the transport of body fluids that leading to an accelerated healing process.

Due to its aforementioned properties, porous Ni-Ti SMA has been used as artificial bones or tooth roots, cranial-facial prosthesis and tools in medicine.

II. EXPERIMENTAL

In the present study, two methods, i.e., conventional powder sintering (CPS) and combustion synthesis (CS), are conducted to produce porous Ni-Ti SMAs. In the CPS, elemental Ti and Ni powders, both smaller than 74µm, were used. TiH_2 (smaller than 44µm) was originally expected to act as a pore-forming agent and to improve the open-pore ratio. Four kinds of equiatomic Ni/Ti blended powders with different TiH_2 additions were designed (Table I). The ball-milled powder mixture was cold pressed at a pressure of 70MPa. Then the powder compacts were sintered at various temperatures for 1h or for various times at 950 ℃ in a vacuum furnace (1.33×10^{-2}Pa). In the CS method, the reactant powders of Ti and Ni were mixed at the equiatomic Ni/Ti composition. The blended powders were pressed into cylindrical pellets with different diameters. The relative density of the pellets was about 42 vol.% of theoretical value. The pellets were then put into a tube furnace with certain pre-heating temperature and ignited. X-ray diffraction (XRD), DSC, optical micrography and SEM were used to analysis the microstructure and phase transformation.

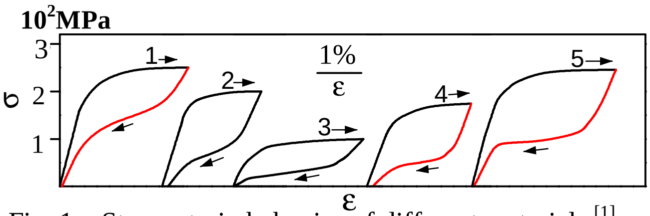

Fig. 1—Stress-strain behavior of different materials.[1]

III. RESULTS AND DISCUSSION

Porous Ni-Ti SMAs have been successfully fabricated with CPS and CS. The microstructure, XRD, phase transformation, mechanical properties and stress-strain behavior of porous Ni-Ti SMAs have been studied.

Table I. Chemical composition of the blended powders used in CPS (wt.%)

Sample	Chemical Composition (wt. %)		
	Ti	TiH_2	Ni
1	44.9	0.0	bal.
2	35.8	9.3	bal.
3	17.8	27.8	bal.
4	0.0	45.9	bal.

A. *Microstructure*

As can be seen from Table II, by using the two methods, we obtained two kinds of porous Ni-Ti SMAs

Table II. The porosity, open-pore ratio and pore size of porous Ni-Ti SMAs

Producing method	Porosity, %	Open-pore ratio, %	Pore size, μm
CPS	30～40	>95	<100
CS	60～70	>90	-

with porosity of 30～40 vol.% and 60～70 vol.%, respectively. All porous Ni-Ti SMAs have a high open-pore ratio, which means that almost all pores are interconnected.

From Figure 2, we can see that the pores in SMAs produced by CPS are small and irregularly shaped. With increasing addition of TiH_2, the pores become smaller and the pore distribution becomes more homogeneous. These are due to the small size of TiH_2 powder and the great reactivity of new-born Ti that decomposed from TiH_2.

Figure 3 shows the macrograph, optical micrograph, and SEM of the combustion-synthesized porous Ni-Ti SMAs. As can be seen, each synthesized Ni-Ti SMAs has developed a three-dimensionally interconnected network of pores and channels during CS of elemental powders. This porous network, it should be noted, is particularly suitable for implant fixation by tissue rapid ingrowth which offering distinct advantages over other methods for achieving secure tissue (and particularly bone)-to-implant fixation as suggested by a recent study.[3]

B. *XRD analysis*

Figure 4 shows the XRD results of samples produced

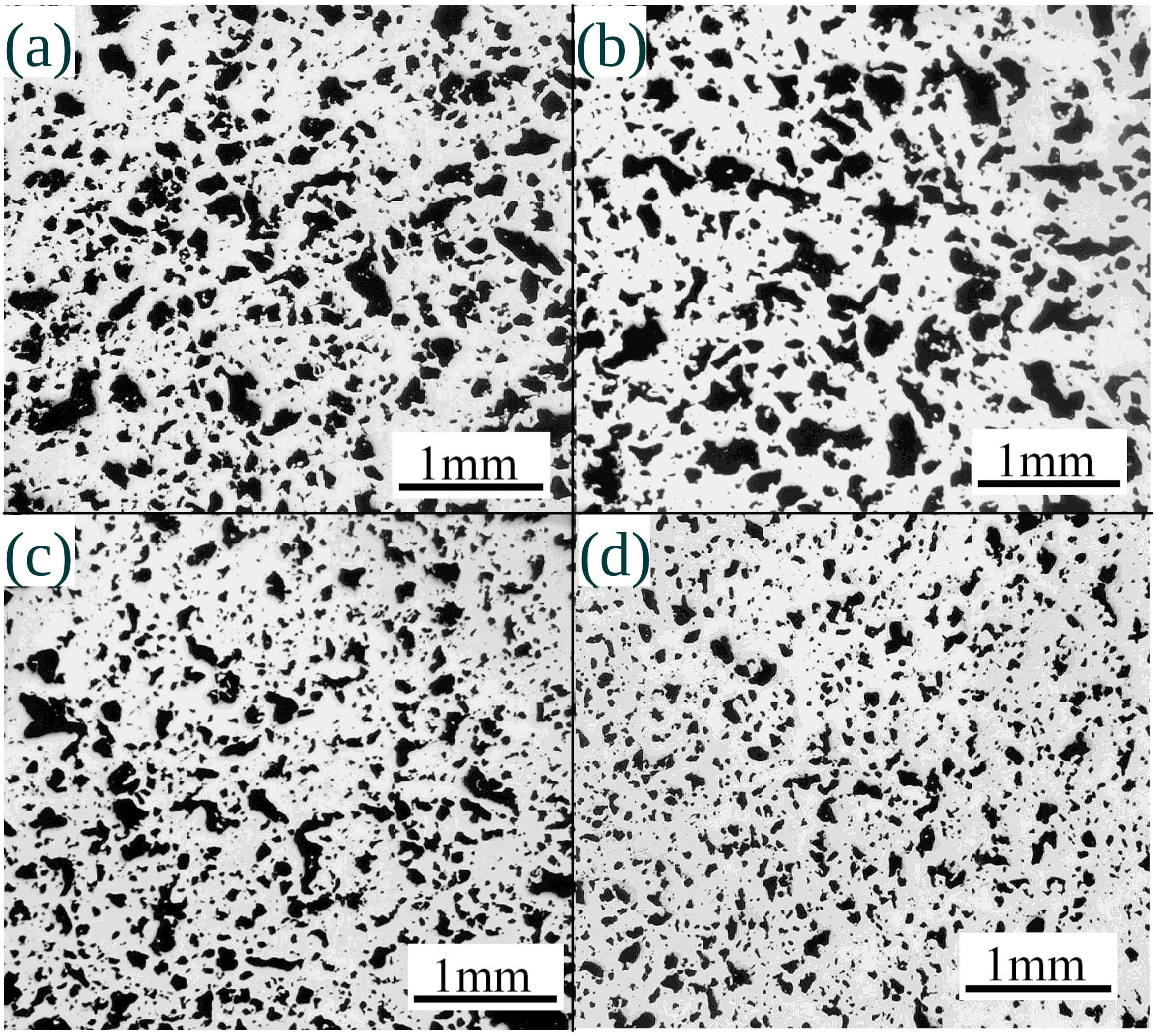

Fig. 2—Optical micrographs of porous Ni-Ti SMAs produced by CPS: (a) 1#, (b) 2#, (c) 3#, (d) 4#.

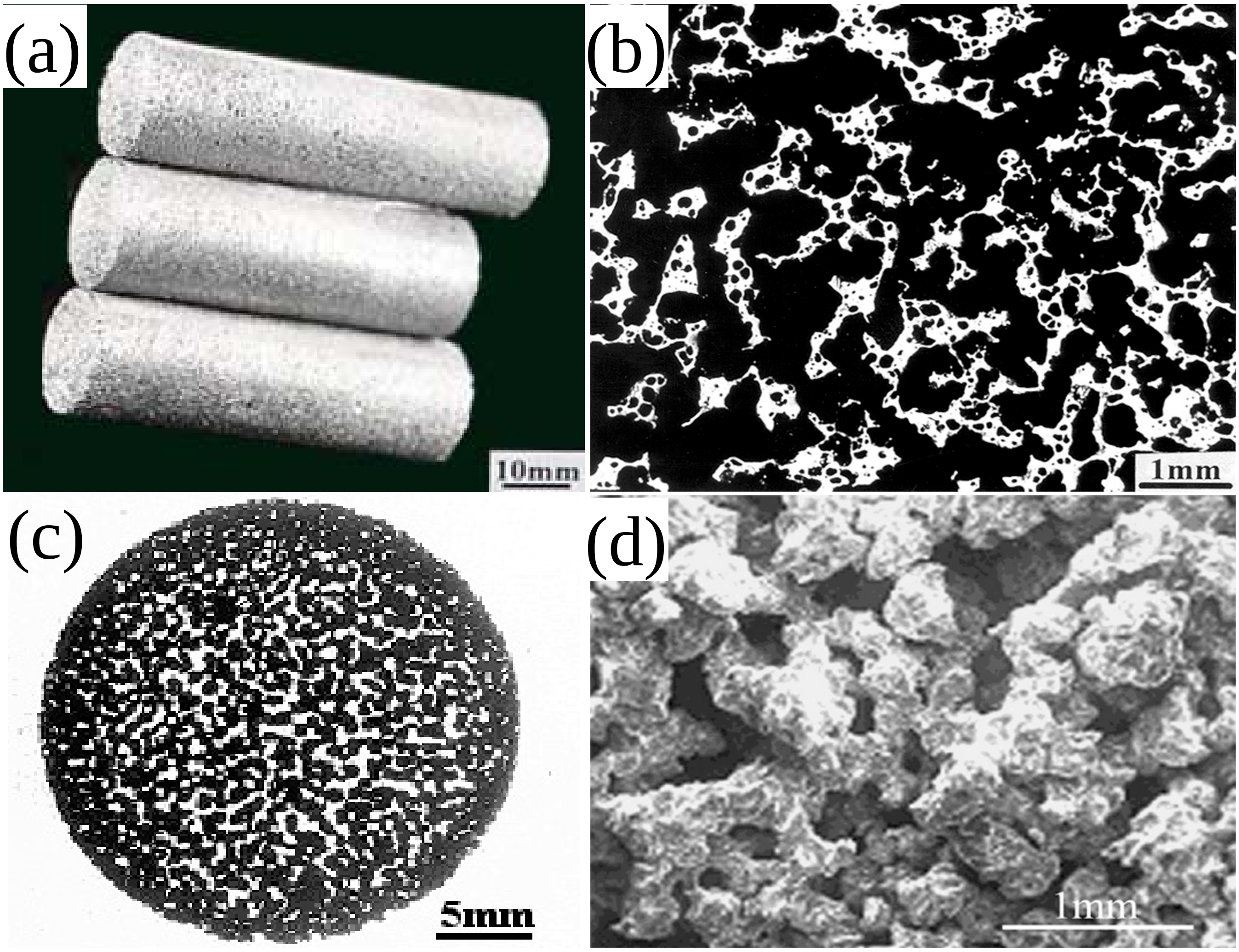

Fig. 3—Porous Ni-Ti SMAs synthesized by CS: (a) macrograph, (b) optical micrograph, (c) a cross-sectional slice, and (d) SEM micrograph.

by CPS. As can be seen, the sintering conditions (sintering temperature and sintering time) significantly influence the phases in the sintered porous Ni-Ti SMAs. At lower sintering temperatures (e.g., 750℃), Ni_3Ti is the dominate phase in the experimental alloy and pure Ni as well as pure Ti exists. With increasing sintering temperature and sintering time, NiTi phase increases greatly in contrast to the decrease of Ni_3Ti. This is because the self- and inter-diffusion of Ni and Ti are improved by increasing sintering temperature and sintering time, and more NiTi phase forms due to the Ni/Ti equiatomic stoicheomitric relationship of all four powder compacts.

As shown in Figure 5, the CS process results in the formation of 100% intermetallic compounds. The dominant phases, B2(NiTi) and B19(NiTi), are presented in every case, and Ti_2Ni, Ni_3Ti, and Ni_4Ti_3 are also observed. Because of the low exothermic character of the reaction between Ti and Ni, to synthesize Ni-Ti SMAs by CS, pre-heating is needed.[4] As can be seen from Figure 5, B19(NiTi) increases while B2(NiTi) and Ni_4Ti_3 decrease with increasing pre-heating temperature due to the greater heat, which improves the inter- and self-diffusion between Ni and Ti, with increasing pre-heating temperature.

Obviously, the following reactions probably take place during CPS or CS:

$$Ni + Ti \rightarrow NiTi + 67kJ/mol \qquad (1)$$

$$Ni + Ti \rightarrow Ti_2Ni + 83kJ/mol \qquad (2)$$

$$Ni + Ti \rightarrow Ni_3Ti + 140kJ/mol \qquad (3)$$

$$TiH_2 \rightarrow Ti + H_2 + 144kJ/mol \qquad (4)$$

$$Ni + Ti \rightarrow Ni_4Ti_3 + heat \qquad (5)$$

All of these reactions are exothermic in nature with the heats as indicated. With the great heat released from reaction (4), the self- and inter-diffusion, which generates Kirkendall pores, between Ni and Ti are improved during the CPS and contributed to the pore shrinkage, the increase of pore number and the increase of NiTi phase. Therefore, the pores become smaller and the pore number increases with increasing TiH_2 addition. With the reaction heat released from reactions (1)～(4) and the heat provided by pre-heating, the CS process becomes self-sustaining.

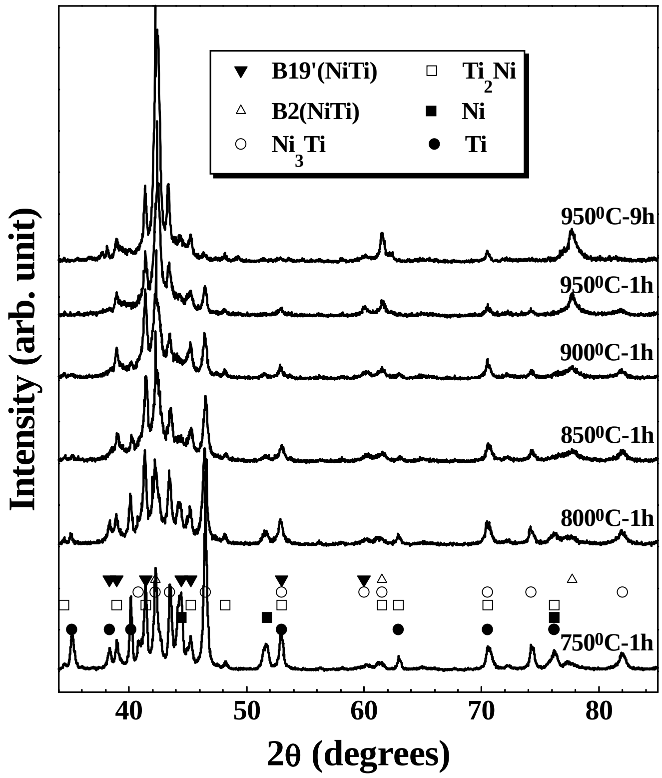

Fig. 4—XRD results of porous Ni-Ti SMAs produced by CPS.

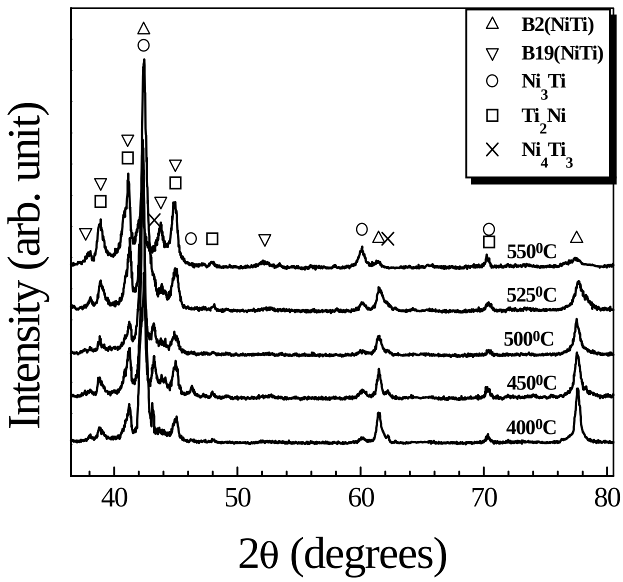

Fig. 5—XRD results of porous Ni-Ti SMAs produced by CS.

From the XRD results shown in Figure 4 and Figure5, it can be found that NiTi, Ni_3Ti and Ti_2Ni always exist in both of the methods. This can be explained by looking at the phase diagram of Ni-Ti and noting that these three phases are stable. Moreover, reactions 2 and 3 are more thermodynamically favored than reaction 1. Thus, Ni_3Ti and Ti_2Ni are difficult to remove completely just by changing the sintering conditions or pre-heating temperature.

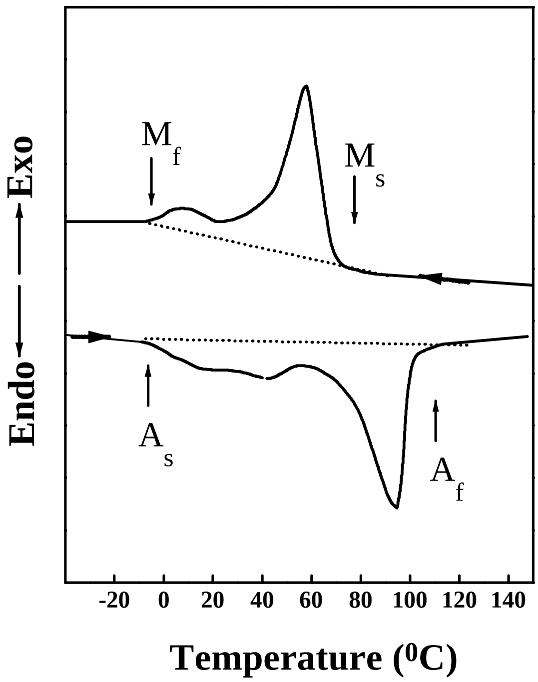

Fig. 6—Schematic DSC curve of porous Ni-Ti SMAs fabricated by CPS.

Table III. The Young's moduli and ultimate compressive strength of porous Ni-Ti SMAs produced by CS

Pre-heating temperature, ℃	400	450	500
porosity, %*	65.6	59.2	63.0
Young's modulus, GPa	1.08	2.59	2.21
Compressive strength, MPa	67.8	78.4	76.8

* Porosity of the samples for testing Young's modulus

C. *Phase transformational behavior of porous Ni-Ti SMAs*

Figure 6 represents the typical DSC curve of porous Ni-Ti alloys produced by CPS. One can easily recognize that the thermal peaks are much broader and two peaks overlap under both heating and cooling conditions. This phenomenon has also observed to appear in some Ni-Ti film and Ni-Ti-Hf high temperature SMAs. This phenomenon here is thought due to the microcompositional difference, which affects the transformation temperatures of Ni-Ti greatly, existing within individual sintered grains since the sintering is based on elemental materials and slight concentration may exist within the newly formed grains.[5] The characteristic transformation temperatures (℃) for sample 4# sintered at 950℃ for 9h revealed by DSC are: A_s, -8.2℃; A_f, 105.3 ℃; M_s, 69.7℃; M_f, -5.8℃.

D. *Mechanical properties of porous Ni-Ti SMAs*

The Young's modulus and strength are very important in the design of load-bearing implants. The

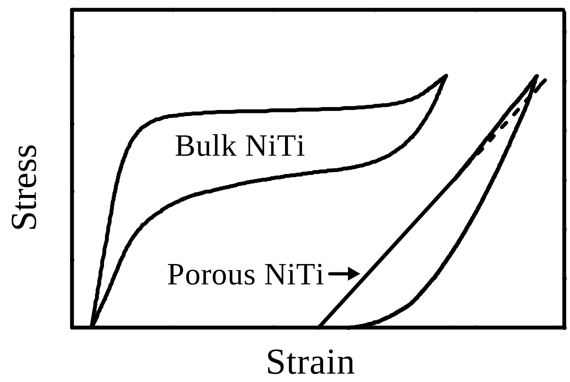

Fig. 7—Typical stress-strain curves of porous and bulk Ni-Ti SMAs.

porosity, Young's modulus and ultimate compressive strength of porous Ni-Ti SMAs produced by CS are listed in Table III. Both the Young's modulus and ultimate compressive strength decrease with increasing porosity. This is in accordance with other porous metals.[6] Compared to other biomaterials, such as dense Hydroxyapatite and Hydroxyapatite-coated Ti, the Young's moduli of the present porous materials are quite close to that of cancellous bone because in the case of the cancellous bone, the Young's modulus and compressive strength are in the range of 1-2Gpa and 1-100MPa.[7] For artificial bones, similar Young's modulus and with mechanical properties the same or better than the natural bone is required. Therefore, the present products can match the replaced cancellous bone in these aspects.

E. *Stress-strain behavior of porous Ni-Ti SMAs*

Figure 7 shows the typical stress-strain behavior of porous and bulk Ni-Ti alloys which exhibit PE. As can be seen, both porous and bulk Ni-Ti alloys have good PE although there is no stress plateau in the porous one. Moreover, comparing to normal porous materials, the porous Ni-Ti alloys have high strain recovery and their deformation resistance increases dramatically with further strain after the elastic deformation stage during compression.

IV. CONCLUSIONS

The present study has examined the micrograph, phase transformation, mechanical property and stress-strain behavior of porous Ni-Ti SMAs produced by CPS and CS. We can conclude that:

(1) Porous Ni-Ti SMAs, with porosity of 30~40 vol.% and 60~70 vol.%, have been successfully fabricated by CPS and CS;
(2) From the XRD spectra, it is found that the phases in porous Ni-Ti SMAs are greatly influenced by the sintering conditions and the pre-heating temperature, and Ti_2Ni and Ni_3Ti phases are difficult to remove completely in both CPS and CS methods;
(3) There exists two-peak phenomenon in the DSC curves of porous Ni-Ti SMAs produced by CPS;
(4) The Young's modulus and compressive strength of the porous Ni-Ti SMAs produced by CS decrease with increasing porosity and the Young's moduli are quite close to that of cancellous bone.

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