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The influence of addition of TiH_2 in elemental powder sintering porous Ni–Ti alloys

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Abstract

TiH_2 powder is added as a pore-forming and active agent in synthesis of porous Ni–Ti alloys by using a conventional powder sintering technique. The influence of addition of TiH_2 on microstructure, memory characteristics and pseudoelasticity (PE) of porous Ni–Ti alloys is investigated. It is found that porous Ni–Ti alloys produced with or without addition of TiH_2 exhibit good memory effect and PE, and the addition of TiH_2 not only has a pronounced effect on the microstructure but also increases the shape memory effect (SME) and volume memory effect of porous Ni–Ti alloys. Further, the addition of TiH_2 has a significant influence on the elastic behavior and Young's modulus of porous Ni–Ti alloys.

Keywords: Porous Ni–Ti alloys; Memory effect; Pseudoelasticity

1. Introduction

Increasing numbers of application of Ni–Ti shape memory alloys, which have excellent mechanical properties, good corrosion resistance and shape memory effect (SME), along with biocompatibility [1,2], have been developed in the past two decades. Recently, porous Ni–Ti alloys have received great interest as a kind of promising biomedical alloys for use in bone implant surgery or in the substitution of defect tissues (e.g. cranial-facial defect prosthesis), due to their porous structure allowing the ingrowth of bone tissues and obtaining a firm fixation of the implants, and also due to their special deformation behavior, i.e. pseudoelasticity (PE), which is similar to that of organic tissue [3].

Normally, the application of Ni–Ti alloys has been limited by their high cost resulted from complicated melting and machining procedures, and the high Young's moduli and yield stresses of dense materials also limit their applications in medicine. On contrast, powder metallurgy (PM) is a method for producing products with net final shape and omitting many machining processes. By obtaining various porosity, pore shapes and pore sizes through controlling the compacting and sintering conditions, it is easy to adjust the Young's moduli and yield stresses of porous alloys by PM technique to match those of replaced organs. Therefore, PM has received great interest in the preparation of porous Ni–Ti alloys. However, most of present studies on preparation of Ni–Ti alloys [4–7] by powder sintering technique focus not on the medical porous ones, but on obtaining dense Ni–Ti alloys with or without a subsequent treatment [8]. The lack of comprehensive reports on the porous Ni–Ti materials produced from powder sintering is one main motivation of this paper.

In order to obtain porous materials, pore-forming agents like hydrides are frequently added to the blend [9]. In the present work, TiH_2 is added as a reactant and pore-forming agent in producing porous Ni–Ti alloys, and it is expected that the addition of TiH_2 can reactivate the sintering process and improve the SME and PE of porous Ni–Ti alloys.

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Table 1
Chemical composition of the experimental blended powders (wt.%)

Sample No.	TiH_2	Ti	Ni
1	0	44.9	Balance
2	9.3	35.8	Balance
3	27.8	17.8	Balance
4	45.9	0	Balance

2. Experimental

Elemental Ti (<74 μm), Ni (<74 μm) and TiH_2 (<44 μm) powders were employed in the present study. Four kinds of equiatomic Ni–Ti blended powders with different TiH_2 content were designed to assess the influence of addition of TiH_2 on sintering behavior. Table 1 shows the nominal composition of blended powders. The blended powders were uniaxially compacted under a pressure of 70 MPa after mixed by ball-milling for 2 h in an Ar atmosphere. The compacts were then isochronal sintered at various temperatures for 1 h or isothermal sintered at 1223 K for various times. It was found experimentally that TiH_2 decomposes at about 823 K, so in order to have a better solid-state diffusion and attempt to improve the porosity by the decomposition of TiH_2, two heating rates were used during sintering: a slow heating rate of 4 K min^{-1} to 773 K followed by a fast heating rate of 30 K min^{-1} to the desired final sintering temperature.

Compression test was used to determine the SME and PE of sintered porous Ni–Ti alloys. During compression test, the sintered cylindrical specimens were compacted along the axial at a constant strain rate of 8.8×10^{-4} s^{-1} at ambient temperature. The diagrams of stress–strain for each case were recorded with the aid of DCS-10t Instron testing machine. The slope of the linear deformation stage during compression was used to present qualitatively the Young's moduli of the materials. After compression the specimens were heated to 473 K to determine the memory effect and PE. Optical metallography, scanning electron microscopy (SEM) and IPS-500 Image Analysis were performed for microstructural characterization analysis, and the open porosity and general porosity were measured by the method stated in the literature [10].

3. Results

3.1. General porosity and open-pore ratio

Table 2 shows the general porosity and open-pore ratio of the sintered porous alloys produced from different TiH_2 addition. The open-pore ratio is defined as the ratio of the open porosity to the general porosity. As can be seen, the general porosity and open-pore ratio tend to decrease with increasing addition of TiH_2. We can conclude that TiH_2 is not an ideal pore-forming agent in sintering consolidation of porous Ni–Ti alloys in the present study.

3.2. Microstructural evolution

It is found that the pore shape and pore size vary greatly with addition of TiH_2. Sintered at 1223 K for 9 h, the pore distributions are shown in Fig. 1. As can be seen, with increasing TiH_2 addition, the pores become smaller, the pore number increases, and the pore distribution becomes more uniform. Further, the inset pictures show that the difference between the centers, where have the largest pores, and other areas of the sintered alloys decreases with increasing addition of TiH_2. The corresponding pore size distributions obtained by means of image analysis are shown in Fig. 2. The average pore size of sample 1–4 sintered at 1223 K for 9 h is 95, 92, 68 and 61 μm, respectively. Obviously, with increasing addition of TiH_2, the average pore size decreases, the pore size range as well as the size difference among pores becomes smaller, and the number of small pores increases.

Table 2
The general porosity and open-pore ratio of samples sintered at different temperatures for 1 h or at 1223 K for 9 h (%)[a]

Sintering condition		GRP	1023 K	1073 K	1123 K	1173 K	1223 K	1223 K–9 h
1	GP	47.7	41.5	40.3	39.0	37.6	37.8	36.0
	OPR	–	98.4	97.2	97.3	96.6	97.6	99.6
2	GP	47.7	39.5	37.9	38.1	38.1	37.1	36.3
	OPR	–	97.0	97.0	97.6	96.6	97.6	98.3
3	GP	49.8	38.0	36.9	37.6	36.0	36.3	35.9
	OPR	–	97.9	97.6	98.5	96.6	97.2	96.5
4	GP	50.1	36.0	34.9	34.8	33.9	34.3	32.6
	OPR	–	97.2	95.3	96.3	94.5	94.7	95.9

[a] GRP, green porosity; GP, general porosity; OPR, open-pore ratio.

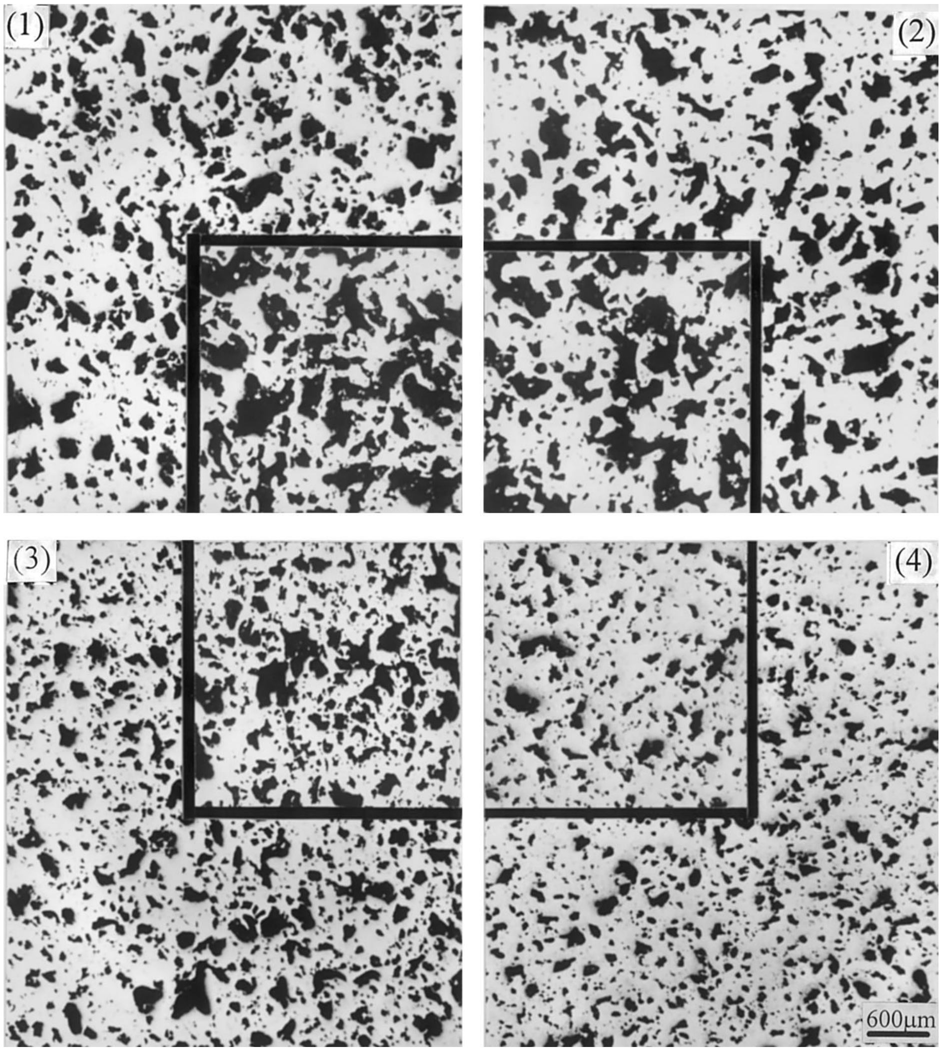


Fig. 1. The optical micrographs sintered at 1223 K for 9 h with different TiH_2 addition. The insets are the center areas of sintered samples whose pore sizes are different the most from other areas. (1) 1; (2) 2; (3) 3; (4) 4.

3.3. Deformation behavior and PE of sintered porous Ni–Ti alloys

Fig. 3 shows the stress–strain curves of porous Ni–Ti alloys with different addition of TiH_2 under pre-strain of 8%. In these curves, the PE associated with the martensitic transformation appears in each sample. As can be seen, the addition of TiH_2 has complex influences on the deformation behavior of porous Ni–Ti alloys. Sintered during 1023 and 1173 K, with increasing TiH_2 addition, the elastic deformation and Young's modulus of linear deformation stage increase. Also the curve width of stress–strain hysteretic loop decreases with addition of TiH_2. And the trends weaken with the increase of sintering temperature. After sintering at 1223 K for 1 h, the parameters (elastic deformation, Young's modulus and hysteretic loop width) change little with addition of TiH_2. On the contrary, the elastic deformation and Young's modulus decrease while the hyteretic loop width increases with increasing addition of TiH_2 after further increasing sintering time (9 h) at 1223 K. Another feature of these stress–strain curves is that the Young's modulus of each sample after sintered above 1173 K increases with increasing strain after the linear deformation stage.

3.4. Shape and volume memory effect

In the stress–strain curves, the remained strain after deformation is partially or nearly completely recovered by heating the specimen to 473 K, namely porous Ni–Ti alloys exhibit SME. The axial and radial strain recovery of porous Ni–Ti alloys sintered at 1023 K for 1 h are shown in Fig. 4. Obviously, the axial and radial strain recovery increase with increasing addition of TiH_2 after sintered at 1023 K for 1 h.

Accompanying with the shape recovery, the pores tend to recover their original conditions and the initial volumes of porous Ni–Ti alloys recover, i.e. deformation of porous shape memory alloys is accompanied by the macroscopic volume change, which is called VME. Fig. 5a and b are the volume recovery of porous Ni–Ti alloys. One can see that the volume recovery increases greatly with increasing sintering temperature, sintering time, and addition of TiH_2.

4. Discussion

The addition of TiH_2 as a reactant has been found beneficial for the synthesis of porous Ni–Ti alloys. In the present study, the sintering temperature is lower than the temperature to form a liquid phase, thus solid–solid diffusional reactions of the reactants seem to be the dominated sintering mechanism. As the powder sintering technique is known to be susceptible to the formation of Kirkendall pores when sintering elemental powders [5,11], a schematic diagram of the sintering mechanism model is shown in Fig. 6 starting with a representation of the segregated powder structure (Fig. 6a and e). When sintering is performed, non-uniform diffusion takes place (Fig. 6c and f). Since nickel diffuses faster than Ti [11], the Ni particles experience a net loss of atoms and Kirkendall pores are created at the prior Ni sites (Fig. 6d and g), which contribute principally to the new-generated pores in the sintered alloys. The addition of TiH_2 has the following two effects: primarily, the green compact has greater number of pores and more uniform pore distribution with increasing addition of TiH_2 under the same compaction conditions due to the smaller size and smaller density of TiH_2 than Ti powder; secondly, compared to the samples without addition of TiH_2, the new generated Ti (Fig. 6b) that decomposed from TiH_2 at about 823 K is far much more reactive than the original Ti powder, and this new-generated Ti along with the great heat given out by the decomposition of TiH_2 will strengthen the self- and inter-diffusion and thus enhances the sintering degree and contributes to a further increasing number of Kirkendall pores and great shrinkage of the original big pores (Fig. 6d). Therefore, the general porosity and open-pore ratio of the final sintered alloys tend to decrease, the pores become smaller and the pore number and the homogeneity of pore distribution increase with increasing TiH_2 addition.

The improvement of SME of porous Ni–Ti alloys sintered with addition of TiH_2 is associated with the

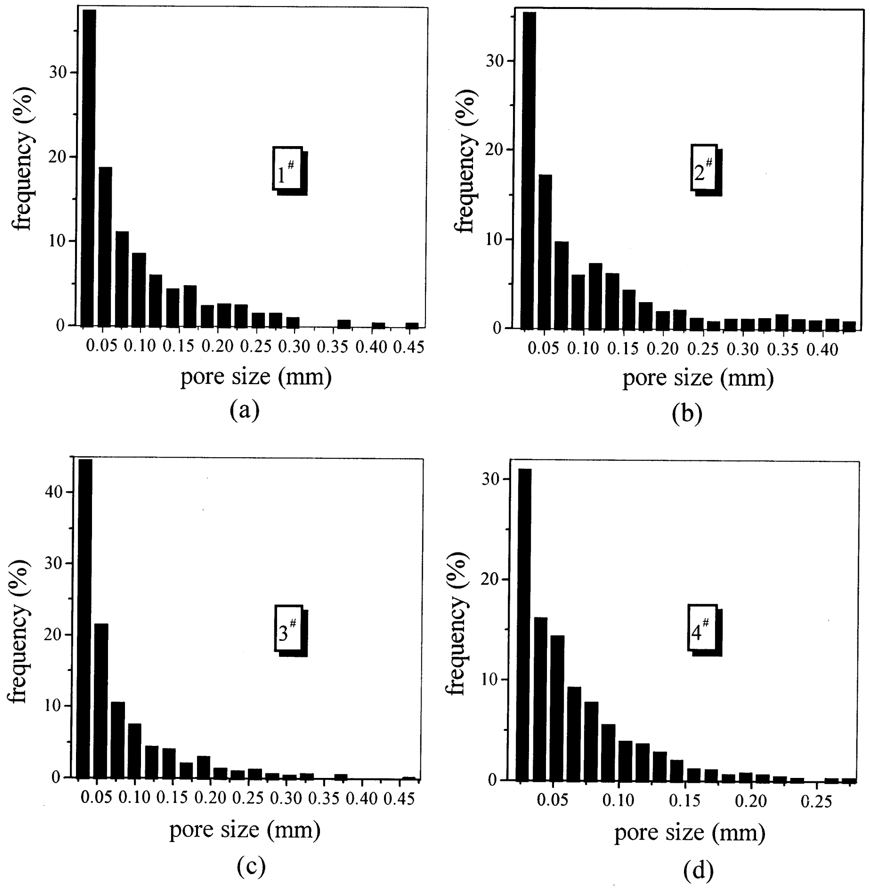
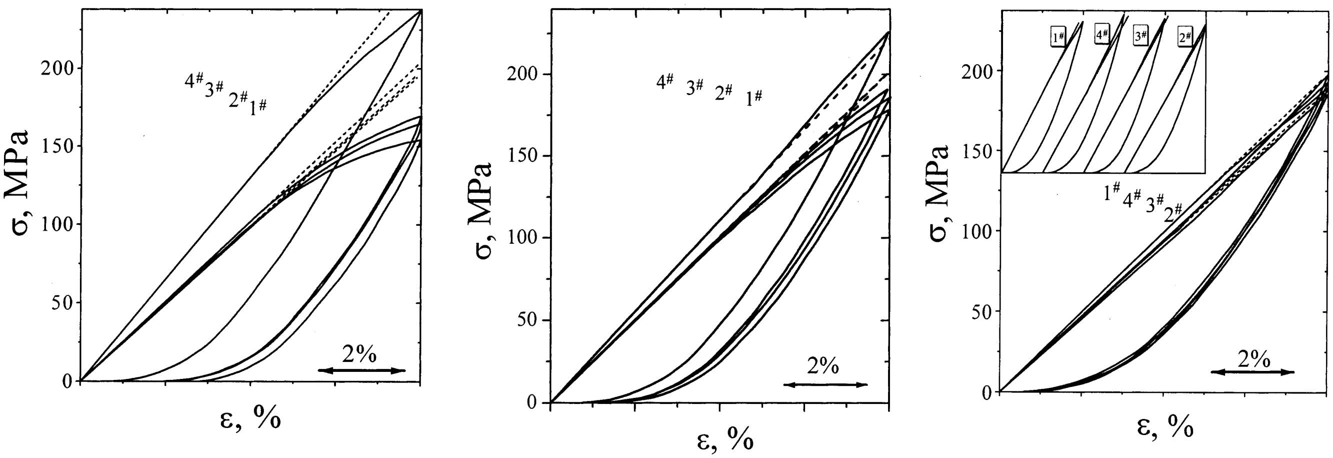


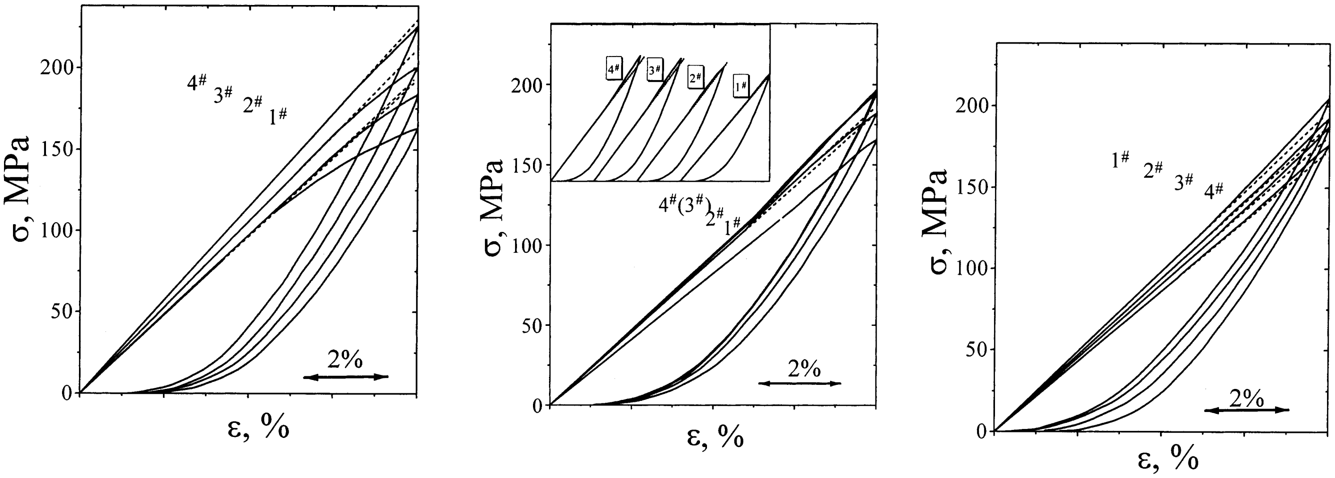
Fig. 2. Pore size distributions of porous Ni–Ti alloys sintered at 1223 K for 9 h with different TiH_2 addition.



(a) 1023K-1h

(c) 1123K-1h

(e) 1223K-1h



(b) 1073K-1h

(d) 1173K-1h

(f) 1223K-9h

Fig. 3. The stress versus strain diagrams of porous Ni–Ti alloys with different TiH_2 addition under different sintering conditions ($\varepsilon_t = 8\%$). Dotted lines qualitatively show the Young's moduli. (a) 1023 K, 1 h; (b) 1073 K, 1 h; (c) 1123 K, 1 h; (d) 1173 K, 1 h; (e) 1223 K, 1 h; (f) 1223 K, 9 h.

microstructure of porous Ni–Ti alloys, this is in accordance with the result obtained by Solonin et al. [12]. It should be noted that the better the SME, the better the VME; also, the more pronounced the PE, the narrower the hysteretic loop width as the width of the hysteretic loops of the stress–strain curves is determined by the dissipation of energy. Obviously, the deformation of porous materials is nonuniform and leads to plastic deformation while decreases elastic deformation. As aforementioned, the addition of TiH_2 enhances the sintering degree, which means the enhancement of plastic deformation resistance; and makes the pore sizes and pore distribution more uniform, which means the enhancement of deformation uniformity. Thus, the plastic deformation decreases while SME and PE increases with addition of TiH_2. In addition, the existence of pores makes the factual deformation of porous materials less than the prestrain (here is 8%) and leads

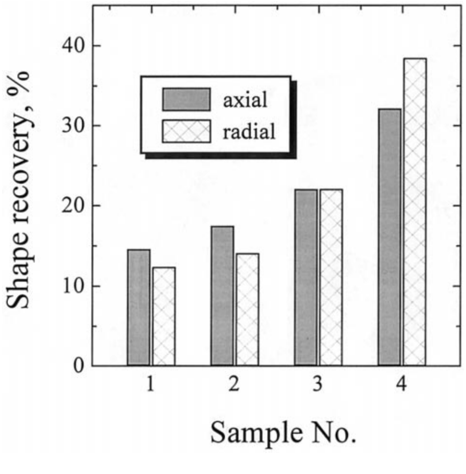


Fig. 4. The shape recovery in axial and radial after prestrain 8% in axial of porous Ni–Ti alloys sintered at 1023 K for 1 h with different TiH_2 addition.

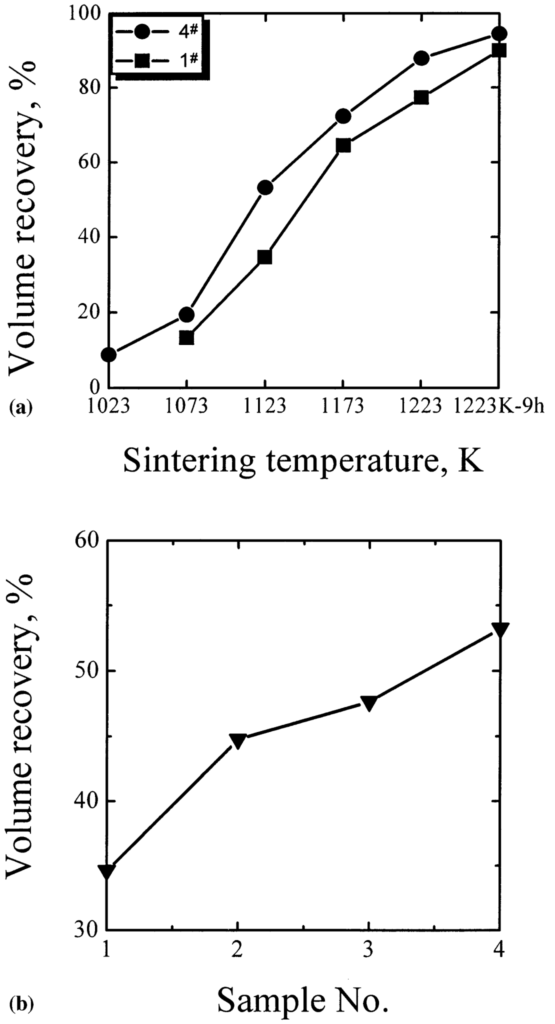


Fig. 5. (a) The volume recovery of porous Ni–Ti materials after sintered at different temperatures. (b) The volume recovery of porous Ni–Ti alloys sintered at 1123 K for 1 h with different TiH_2 addition.

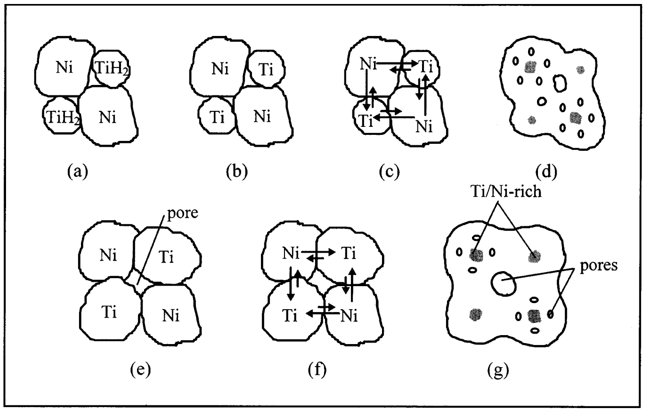


Fig. 6. The schematic diagram of the sintering mechanism model for powder sintering porous Ni–Ti alloys with (a–d) or without (e–g) TiH_2 addition.

to relatively large PE. Therefore, SME, VME, and PE increase while hysteretic loop width decreases with increasing addition of TiH_2. When sintering temperature increases, the sintering temperature is more important in contribution to the self- and inter-diffusion between Ti and Ni, and the influence of TiH_2 addition on the homogeneity of pore sizes as well as pore distribution wanes. Thus at higher sintering temperature, the addition of TiH_2 has less influence on elastic deformation, hysteretic loop width and Young's modulus. However, the reason for the change after sintered for long time (9 h) at 1223 K is not known at this time.

It is known that during cold deformation, the stress of porous materials increases with increasing strain like other normal dense materials. However, the increase rate of stress versus strain after linear deformation stage is larger than that of dense materials, this is probably associated with the decrease of porosity during compression test and the fact that there is stress concentration on the edge of pores. As a result, the Young's moduli of samples after sintered above 1173 K increase with increasing strain after the linear deformation stage.

Moreover, from the stress–strain curves in the present study we can speculate that the Young's moduli and yield stresses of porous Ni–Ti alloys are easier to be adjusted by selecting certain stuffs and sintering conditions, and they are more possible to be adjusted to match those of replaced organs. Also, the good SME and VME of porous Ni–Ti alloys can simplify the implanting process of medical implants and make patients tolerate less pain. Thus, it seems that addition of TiH_2 is preferable in producing porous medical Ni–Ti alloys.

5. Summary and conclusions

The results of this work show that porous Ni–Ti alloys, which exhibit good SME, PE and special VME, can be synthesized with or without addition of TiH_2. The addition of TiH_2 assures a more homogeneous distribution of pores and pore sizes, and with increasing addition of TiH_2 the pore size decreases while the number of small pores increases significantly when sintered at 1223 K for 9 h. Also, the addition of TiH_2 effects both the SME, VME and PE. At relatively low sintering temperatures, the SME and VME increase with increasing addition of TiH_2. Further, the addition of TiH_2 has a complex effect on the elastic behavior, Young's modulus and hysteretic loop width in stress–strain curves, and this effect makes it possible to obtain the desired medical porous Ni–Ti alloys with controllable elastic behavior and Young's modulus, which are important for the match with replaced organs.

Acknowledgements

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Appendix A

The shape recovery (η_S) and volume recovery (η_V) are defined/calculated as following:

$$\eta_S = \frac{\varepsilon_r}{\varepsilon_r + \varepsilon_R} \times 100\%$$

$$\eta_V = \frac{v_3 - v_2}{v_0 - v_2} \times 100\%$$

$$\varepsilon_r = \frac{h_3 - h_2}{h_0} \times 100\%$$

$$\varepsilon_R = \frac{h_0 - h_3}{h_0} \times 100\%$$

where ε_r, ε_R are the reversible and residual strain, h_0, v_0 are the height and volume of sintered samples before compaction, h_2, v_2 are the height and volume of sintered samples after unloading h_3, v_3 are the height and volume of sintered samples after recovery.

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