

Porous NiTi alloy prepared from elemental powder sintering

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An elemental powder sintering (EPS) technique has been developed for the synthesis of porous NiTi alloy, in which Ni and Ti powders are used as the reactants and TiH₂ powder is added as a pore-forming agent and active agent. Effects of various experimental parameters (sintering temperature, sintering time, and TiH₂ content) on the porosity, pore size and pore distribution as well as phase composition in experimental alloys are investigated. It is found that in order to avoid the formation of carcinogenic pure Ni phase, the porous NiTi alloy should be synthesized over a temperature of 1223 K. This gives NiTi as the main phase without any elemental phase. Substitution of Ti by TiH₂ is more economic and more favorable to obtain homogeneous porous NiTi alloy. A proper selection of initial powders, ball-milling, pressing and sintering process makes it possible to achieve the porous NiTi alloy with desired properties.

I. INTRODUCTION

In recent years porous NiTi shape memory alloy has been acknowledged as one of the most promising biomedical materials for use in bone implants surgery and in the substitution of defect tissue because its porous structure allows the ingrowth of human tissue and is favorable for the fixation of the implant as well as the transport of liquid nourishment. Also because the special superelasticity of NiTi alloy accommodates deformation behavior of organic tissue. Furthermore, porous NiTi alloy has excellent mechanical properties, good corrosion resistance and biocompatibility, along with shape memory effect.¹

There are many reports²⁻⁷ about the preparation of NiTi alloy by powder metallurgy, however most of these studies focus on the homogeneous compact NiTi alloy but not on the medical porous one. The lack of comprehensive reports on the porous NiTi alloy produced from EPS is the main motivation of this paper.

The concept of conventional sintering of elemental equiatomic blends of Ni and Ti powders presents difficulty in achieving homogenization as homogenization by solid state diffusion usually requires a very long time. One means to achieve homogenization is to introduce a liquid phase (Ti-22.4at.%Ni) like the ignition synthesis during sintering, since the existence of liquid phase promotes the kinetics of mass transfer by causing the solid to dissolve. Although the liquid phase provides the means to achieve rapid homogenization of the blended powders, its presence leads to loss of dimensional stability. Hence, the contradictory factors which exist with respect to homogenization and dimensional

stability present a dilemma, since both aspects are essential to achieve an alloy of NiTi with satisfactory desired properties. Another means to achieve homogenization is to heat at elevated temperatures for a very long time, but this leads to the difficulty of accurate controlling of porosity in addition to higher energy consumption. In the present study, the authors used TiH₂ powder to partially or wholly take place of Ti powder for the first time, and it is expected that the decomposition of TiH₂ can accelerate the reactive sintering process and a rapid homogenization can be achieved. From practical point, the TiH₂ is more cost-saving compared with pure Ti and the substitution of Ti by TiH₂ can decrease the oxidization of pure Ti powder, which is more feasible for engineering application.

II. EXPERIMENTAL

Elemental Ti (-74 μ m), Ni (-74 μ m) and TiH₂ (-44 μ m) powders, all with purity of 99%, were employed in the present study. Four kinds of equiatomic NiTi blended powders with different TiH₂ content were designed to assess the influence of addition of TiH₂ on the sintering behavior. Table I shows the nominal composition of the blended powders

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

Sample No.	TiH ₂	Ti	Ni
1 [#]	0	44.9	bal.
2 [#]	9.3	35.8	bal.
3 [#]	27.8	17.8	bal.
4 [#]	45.9	0	bal.

mixed by ball-milling in a steel chamber for 2hr in an argon atmosphere. The specimens were pressed in a uniaxial die press under 70MPa for 2min. The pressed specimens were 11.5mm in diameter and typically 10.3mm in height. The compacts were sintered at various temperatures for 1hr or for various times at 1223 K in a 1.33×10^{-2} Pa vacuum tube furnace. It is 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.

The general porosity of the green/sintered specimens was calculated by the following formula:

$$\varepsilon = \left(1 - \frac{\rho}{\rho_0}\right) \times 100$$

in which ρ and ρ_0 stand for the green/sintered density and its corresponding theoretical density respectively. The green/sintered density was determined from its weight and dimensional measurements. The theoretical density is 6.19 g cm^{-3} (based on the value of pure Ni and pure Ti for equiatomic NiTi powders) for the blended powders and 6.44 g cm^{-3} for the NiTi alloy with its compound structure (B2 type).⁸ The general porosity is composed of two parts, open porosity and closed porosity. The open porosity is determined by the liquid weighing method.⁹ The open porosity-ratio is defined as the ratio of the open porosity to the general porosity.

Specimens were sectioned along a diameter for microstructure examination. IPS-500 Image Analysis was used to measure mean pore sizes and X-ray diffraction (XRD) was used to monitor changes in the crystalline phase.

III. RESULTS

Fig.1 shows the XRD examination of the pressed powders. As can be seen, the three kinds of powders, Ni, Ti and TiH_2 have been just mechanically blended, and no alloying phenomenon has occurred.

The sintered porosity of a compact can be adjusted in the range of 30 ~ 40vol.% by varying the experimental parameters. Tables II and III represent green porosity, general porosity and corresponding open porosity-ratio obtained. It is found that the green porosity, in the range of 47.7~50.1vol.%, increases slightly as the TiH_2 is added while the general porosity and open porosity-ratio decrease evenly with increasing sintering temperature, sintering time and/or TiH_2 content. Furthermore, the open porosity-ratios of all sintered specimens are in excess of 95%, and the sintered general porosity, compared with the green

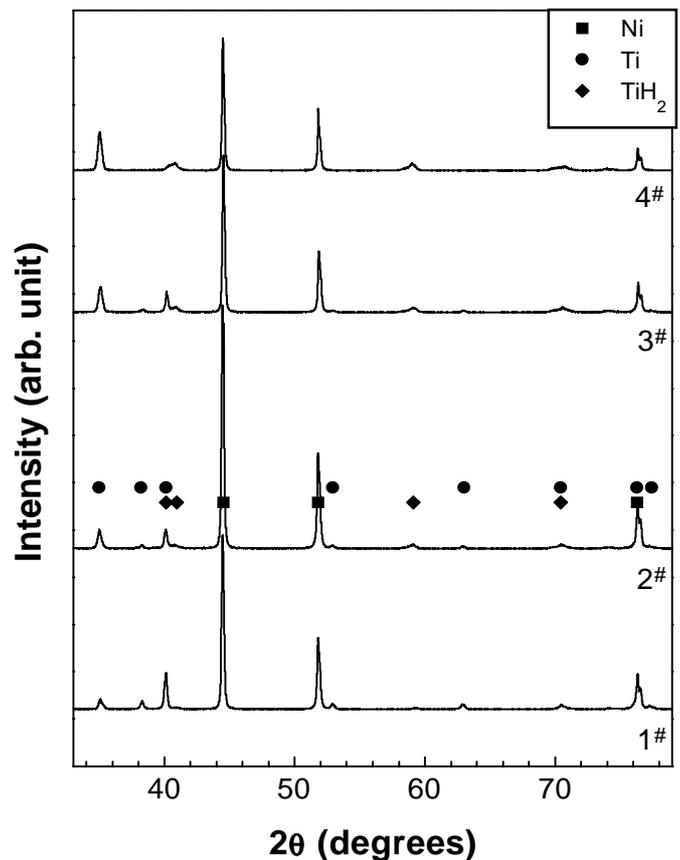


FIG.1 XRD patterns of the samples with no heat-treatment.

Table II. Porosity and open porosity-ratio of samples sintered at various temperatures for 1hr.

Sintering temp.	GRP	1023 K	1073 K	1123 K	1173 K	1223 K
1#	GEP	47.7	41.5	40.3	39.0	37.8
	OPR	—	98.4	97.2	97.3	96.6
2#	GEP	47.7	39.5	37.9	38.1	37.1
	OPR	—	97.0	97.0	97.6	96.6
3#	GEP	49.8	38.0	36.9	37.6	36.3
	OPR	—	97.9	97.6	98.5	96.6
4#	GEP	50.1	36.0	34.9	34.8	33.9
	OPR	—	97.2	95.3	96.3	94.5

GRP: green porosity; GEP: general porosity; OPR: open porosity-ratio.

Table III. Porosity and open porosity-ratio of samples sintered at 1223 K for various times.

Sintering time	GRP	1hr	3hr	5hr	7hr	9hr
1#	GEP	47.7	37.8	35.1	34.4	31.8
	OPR	—	97.6	99.8	98.5	99.8
2#	GEP	47.7	37.1	36.3	34.8	35.7
	OPR	—	97.6	97.9	98.2	98.1
3#	GEP	49.8	36.3	34.6	33.7	33.9
	OPR	—	97.2	97.3	97.2	97.5
4#	GEP	50.1	34.3	33.4	31.3	31.4
	OPR	—	94.7	97.7	94.5	94.4

GRP: green porosity; GEP: general porosity; OPR: open porosity-ratio.

porosity, is markedly smaller, especially for the samples with addition of TiH₂.

In addition, it is found that the TiH₂ content has an important influence on the pore size and distribution. With increasing TiH₂ content, the mean pore sizes of porous NiTi alloys sintered at 1223 K-9hr are 94.5μm, 92.1μm, 67.9μm, and 60.7μm respectively. Fig.2 are typical optical photographs of porous NiTi alloys sintered at 1223 K-9hr. As can be seen, the pore profile appears irregular in character. With increasing TiH₂ content the pore size and the size difference among pores become smaller, while the pore profile becomes more regular. As a result, the pore number increases and the pore distribution is more homogeneous.

The increase of sintering temperature, sintering time and/or TiH₂ content has been found beneficial for the synthesis of porous NiTi alloy, especially the increase of sintering temperature. Fig.3 shows XRD pattern for specimens sintered for 1hr at various temperatures. After sintering at 1023 K-1hr, XRD peaks for Ni, Ti, Ni₃Ti, Ti₂Ni and NiTi (B2 and B19') are present, however Ni₃Ti is the predominant phase, with a few elemental phases. As the temperature is raised above 1023 K, the Ni-rich and Ti-rich phases decrease extensively and the intensity for the peaks of NiTi phase increase. At 1223 K the elemental peaks (Ni and Ti) vanish and NiTi becomes the main phase with small amount of other intermetallic phases. Fig.4 shows the XRD pattern for specimens sintered at 1223 K-9hr with different TiH₂ content. As can be seen, with increase of TiH₂, the intensity for the peaks of the Ni-rich and Ti-rich phases further decreases while that for the peaks of NiTi increases. However, the peaks of Ni₃Ti and Ti₂Ni still appear.

IV. DISCUSSION

The high green porosity, being about 50vol.%, is due to the comparatively low pressing pressure of 70MPa. In comparison, green porosity down to 20% along with sintered porosity just in the order of 12% has been achieved with higher pressures of 155~929MPa.^{4-6,10} With increasing TiH₂ content the green porosity increases. This is because the addition of TiH₂ has two contradictory influences on the green porosity. On the one hand, the TiH₂ powder is smaller than the other two powders (Ni and Ti powders), which results in lower porosity. On the other hand, the low density of TiH₂ compared with pure Ni and Ti results in higher porosity. The latter influence must be a little predominant since increasing TiH₂ content causes the green porosity increase slightly.

In the present study, the sintered porosity is much lower than the green porosity. This large drop in porosity is likely due to the shrinkage of the original pores during sintering. With increasing sintering temperature or sintering time, the shrinkage of the original pores increases, thus the sintered porosity decreases. In addition, from Tables II and III, further increasing sintering temperature above 1073 K or further increasing sintering time over 3hr at 1223 K, the sintered porosity no longer decreases due to the balance of the shrinkage of the existing pores and the generation of pores by Kirkendall effect that results from the different diffusion rate of Ni and Ti. Thus, in view of the sintered porosity obtained, sintering temperature and sintering time can be further increased in accordance with desires of strength, toughness or other properties with the same porosity.

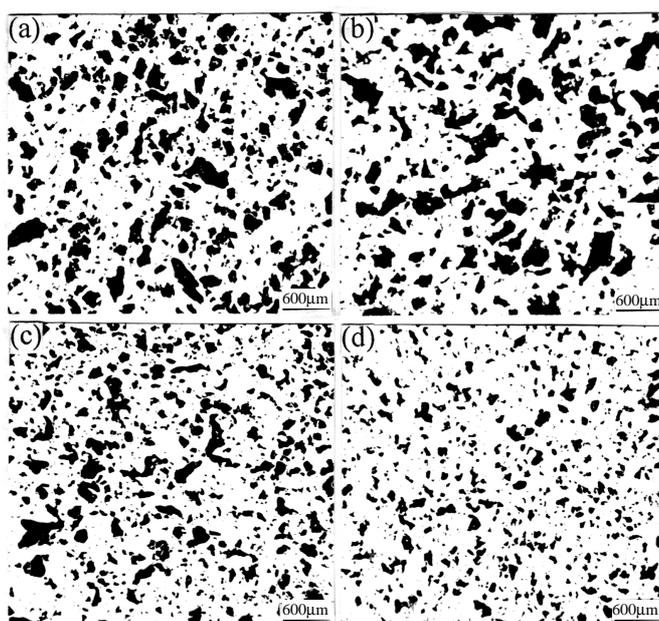


FIG.2 Microstructure of porous NiTi alloy sintered at 1223 K for 9hr: (a) 1[#], (b) 2[#], (c) 3[#] and (d) 4[#].

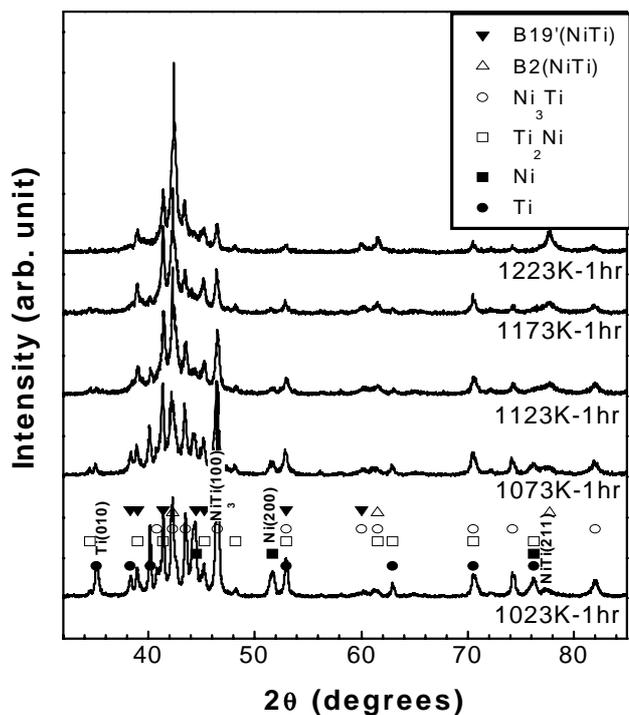


FIG.3 XRD profiles of NiTi compacts after sintering for 1hr at the specified temperature.

It is necessary to note that implants in medicine should have a structure similar to the organic tissue to be replaced. Since the bone tissue of organism is porous and liquid-permeable, it is desirable that the implant material should have the similar open porous structure. In the present study, the open porosity-ratio is over 95%, even reaches 100%. This high open porosity-ratio ensures an open structure of the material and has advantages as follows: primarily it allows the ingrowth of hard bone tissue into the body of the implant and provides the desirable firm fixation by a mechanical bond due to ingrowth of organic tissue into the implant, along with a chemical compound due to interaction between the organism tissue and the component of the implant; secondly the liquid nourishment can penetrate this open structure by capillary effect, which results in better healingness than bulk materials. However, the reason for the high open porosity-ratio in the experimental specimens is not very clear at present time. This high open porosity-ratio is probably related with the degasification and the volatilization of the impurities in the blended powders under high temperature. Moreover, as a consequence of the high heating rate above 773 K, a much higher internal pressure compared with the external pressure may occur and this sudden pressure difference may also enhance the open porosity-ratio.

With increasing TiH_2 content, the pore size is observed to decrease from $94.5\mu\text{m}$ to $60.7\mu\text{m}$ and the size differences among pores tend to be smaller, but the

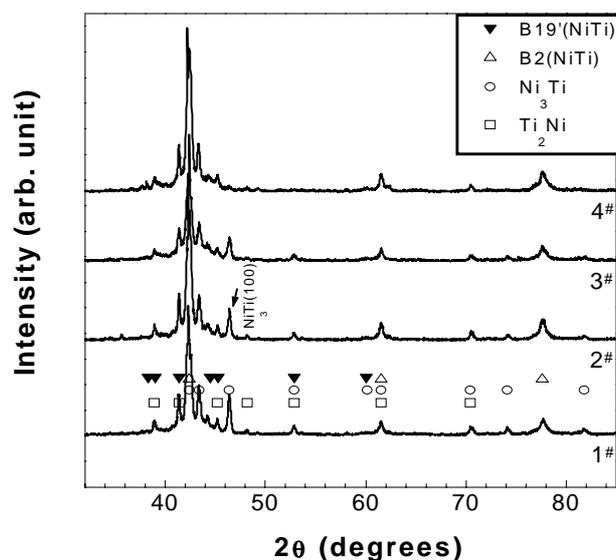


FIG.4 XRD profiles of NiTi compacts after sintering at 1223 K for 9hr.

number of pores increases and the pore distribution is more homogeneous as well as the pore profile more regular. The reason for these phenomena is based on two aspects: first, the smaller TiH_2 powder ($\sim 44\mu\text{m}$) usually exists in the gaps formed by Ni ($\sim 74\mu\text{m}$) and Ti powders ($\sim 74\mu\text{m}$) and the pore size formed from TiH_2 is smaller than that for Ni and Ti powders. As a result, the number of pores is increased and the pore size in sintered alloys becomes smaller as the pores formed by smaller powder are generally characterized by higher shrinkage during sintering;¹¹ secondly, the decomposition of TiH_2 is an exothermic reaction and the new-born Ti is more active which both accelerates the shrinkage of pores and generates more pores as the diffusion rate of new-born Ti is higher than that of the Ti powder used in this experiment.

As a consequence of ball-milling, no alloying phenomenon occurred during the milling process. This is probably due to the slow milling rate and relatively short milling time, which are not enough to result in solid state reaction. However, during sintering both self- and heterogeneous diffusion occurs which results in alloy formation. Since the powder particles are so large that each one contains thousands of the same atoms and it is unavoidable that local composition fluctuation exists in the experimental alloy, formation of Ni-rich and Ti-rich phases result. Furthermore, according to calculations of the Gibbs free energy (table IV), under the present experimental conditions, Ni_3Ti is the most stable phase and NiTi is the least stable phase of the three equilibrium intermetallic phases (Ni_3Ti , Ti_2Ni and NiTi). Therefore Ni_3Ti as well as Ti_2Ni always exists and it seems difficult to obtain a final equilibrium structure of NiTi alone just by solid state diffusion.

It is found that the phases in the porous NiTi alloy obtained are significantly influenced by experimental parameters. From the XRD pattern the 1023 K-1hr sample appears inhomogeneous with Ni, Ti, Ti₂Ni, Ni₃Ti and NiTi phases. However, at 1223 K, NiTi is the dominant phase accompanied by few Ni₃Ti and Ti₂Ni phases, but pure Ni and Ti phases have vanished. Thus, from the medical point, higher temperature sintering is necessary to remove the pure Ni carcinogen. Furthermore, the existence of pure Ni and Ti can also make it difficult to control phase transformation temperature in experimental alloy. It is well known that the diffusion rate is determined by the Arrhenius equation in which the temperature is a key factor that influences the diffusion rate. Sintered at lower temperature, such as 1023 K-1hr, the diffusion rate is lower, the bulk diffusion rates of Ni and Ti are $5.5 \times 10^{-15} \text{ cm}^2/\text{s}$ and $7.0 \times 10^{-12} \text{ cm}^2/\text{s}$ respectively, and Ni₃Ti as well as Ti₂Ni is comparatively easy to form and difficult to remove. Therefore, when sintered at 1023 K-1hr, Ni₃Ti is the dominant phase and pure Ti as well as pure Ni exists. However, with increasing sintering temperature the diffusion rate is extensively enhanced. For example, at 1223 K the bulk diffusion rates of Ni and Ti are $1.5 \times 10^{-12} \text{ cm}^2/\text{s}$ and $2.0 \times 10^{-10} \text{ cm}^2/\text{s}$ respectively. Thus the NiTi phase increases and pure Ni as well as pure Ti vanishes. Likewise, with increasing TiH₂ content the diffusion rate is also enhanced due to the higher activity of the new-born Ti. That is to say, with increasing sintering temperature (from 1023 K to 1223 K) and/or TiH₂ content a higher diffusion rate and markedly improved chemical homogeneity are achieved, and the solid state reaction further tends to the equilibrium, i.e. more NiTi phase is formed since the overall stoichiometric composition is equiatomic.

Table IV. Calculated Gibbs free energies for the stable Ni-Ti intermetallic phases (KJ·mol⁻¹).

Sintering temp.(K)	NiTi	Ti ₂ Ni	Ni ₃ Ti
1023	-155.6	-220.0	-319.0
1073	-162.5	-230.2	-332.9
1123	-165.0	-240.7	-347.3
1173	-176.7	-251.4	-362.1
1223	-184.1	-262.4	-377.3

V. CONCLUSION

Using elemental powder sintering, porous NiTi alloy with 30~40vol.% porosity as well as more than 95% open porosity-ratio has been successfully developed. The experimental parameters (sintering temperature, sintering time and TiH₂ content) have a great influence on the porosity, pore size, pore distribution and phase composition in the experimental alloys. The porous NiTi alloy sintered at 1223 K-9hr has homogeneous pore size and pore distribution. X-ray diffraction experimentation shows that the content of different phases in the porous NiTi alloy is significantly influenced by experimental parameters. At lower sintering temperature, such as 1023 K-1hr, Ni₃Ti is the predominant phase in the experimental alloy while pure Ni as well as pure Ti exists. However, at higher sintering temperature, especially with long sintering time (1223 K-9hr), NiTi is the main phase while pure Ni and pure Ti phases disappear. Thus, from the medical point, sintering at 1223 K is necessary due to the carcinogenic nature of pure Ni. Addition of TiH₂ to the reactants is found to be beneficial for the solid state reaction and the pore distribution, since the Ti from the decomposition of TiH₂ has strong activity and can accelerate the sintering process. As a result less energy and shorter time for sintering are needed.

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