

Microstructure and superelasticity of porous NiTi alloy^{*}

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Received July 15, 1998

Abstract The microstructure, porosity, phase composition and superelasticity (SE) in porous NiTi alloys produced by elemental powder sintering are examined by SEM, Image Analysis and XRD. It is found that it is feasible to produce porous NiTi alloy by elemental powder sintering, and the porosity of sintered porous NiTi alloy is in the range of 36.0%—41.5%. The pores are interconnected and the microstructure is sponge-like. Meanwhile, porous NiTi alloy has good SE. XRD patterns show that there is no pure Ni in alloy sintered at 1223 K-9 h. Compared with the biomedical criteria for choice of implanting materials, porous NiTi alloy is satisfying to a great degree.

Key words: powder sintering, porous alloy, NiTi shape memory alloy, superelasticity.

The mechanical deformation behavior of biological materials, which each has a high recoverable strain (more than 2%), is very different from that of common metallic materials and only the SE of shape memory alloys is similar to it [1]. NiTi alloy also has excellent mechanical properties, good corrosion resistance and biocompatibility. Recently, porous NiTi alloy has become a central item of concern as it possesses lots of advantages as follows. The yield stress of bulk NiTi alloy produced from conventional method is very high and difficult to adjust by subsequent heat treatment. While by obtaining various porosity and pore size through controlling sintering conditions, it is easy to adjust the yield stress of porous NiTi alloy to match that of replaced organism. Moreover, the compressibility and porous structure are beneficial for the ingrowth of bone mineralization tissue and fibrous tissue, which makes the fixation of implant much more natural and reliable. The good shape memory effect (SME) and unique volume memory effect [2] can simplify the implanting process of medical implant and make patients suffer less pain. Additionally, porous NiTi alloy can be used together with bulk NiTi alloy to exert complicated function. Because of these features, porous NiTi alloy shows great advantage and medical value over other medical materials in prosthesis and substitution of bone, joint, teeth and other surgery implanting materials [1]. It can be speculated that this biomedical materials, a product of multi-courses, has great exploitation value.

At present time, Russian scientists proceed in the front in research of porous NiTi alloy and its application in medicine, and some other countries also show great interest in this field. China focuses dramatically on research of biomedical materials. In 1997, “the Current Situation and Development Resources of Biomedical Materials” conference was held in China, which was organized by the National Natural Science Foundation of China, Chinese Academy of Engineering, Chinese Academy of Sciences,

^{*} The research was supported by Chinese Academy of Sciences under key program (Grant No. 971524).

“863” Committee for High Technique and Committee for Biomedical Materials. The purpose of this study is to prepare porous medical NiTi alloy and try to make it satisfy the requirement of biomedical materials, and speed the research and exploitation of porous NiTi alloy in China.

1 Experimental details

The Ti and Ni powders, all with purity of 99%, were blended in the ratio 50/50 at. %. The blended powders were then compacted and sintered in a vacuum tube furnace. The detail sintering conditions are as follows: (1) sintered for 1 h at different temperatures: 1023 K, 1073 K, 1123 K, 1173 K, 1223 K. (2) sintered at 1223 K for different time: 1 h, 3 h, 5 h, 7 h, 9 h. It is found [3] that 1223 K-9 h is the optimal sintering condition and thus we focus mainly on porous NiTi alloy sintered at 1223 K-9 h.

The microstructure and phase composition of sintered porous NiTi alloy were examined by SEM, Image Analysis and XRD. The SME and SE were determined by compaction test on DCS-10t Instron testing machine. The porosity and open pore-ratio were determined as the method used in literati [4,5].

2 Results and Discussion

2.1 Porosity and open pore-ratio

The porosity and open pore-ratio dependence of sintering temperature and sintering time are shown in Fig. 1a and b. As can be seen, the porosity of green compact is high up to 47.7%, and this is much higher than the porosity after sintering, which is between 36.0% and 41.5%. This change in porosity is accordance with ordinary sintering densification process. Moreover, the linear decrease of sintered porosity with increasing sintering temperatures at the range 1023 K~1173 K shows that the sintering temperature has a great influence on porosity. With further increasing sintering temperature, the porosity changes little. The open pore-ratio is between 96.6% and 99.8%, which indicates a good pore interconnection of present alloy. This high open pore-ratio is probably associated with the great porosity of green compact and the volatilization of impurities in blended powders during sintering. In medical field, high open pore-ratio is favorable for the penetration of body fluid, transport of liquid nourishments, and regeneration as well as rebuilding of tissue, which shows a better healing than bulk materials. Therefore, the high open pore-ratio of experimental alloy

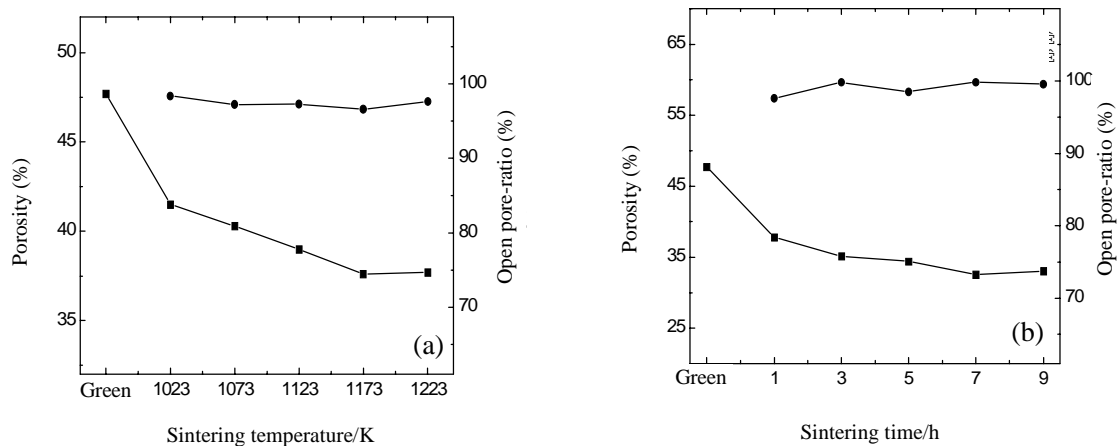


Fig. 1. Dependence of porosity and open pore-ratio on sintering temperature. (b) Dependence of porosity and open pore-ratio on sintering time at 1223K. \circ , Porosity; \bullet open pore-ratio.

satisfies this biomedical requirement. Also, the open pore-ratio does not change obviously with sintering conditions and it is easy to obtain controllable high open pore-ratio in present study.

2.2 Pore size, morphology and distribution

Shown in Fig. 2a and b are micrographs of porous NiTi alloys sintered at 1023 K-1 h and 1223 K-9 h, respectively. One can see that the pore size of porous NiTi alloy sintered at 1023 K-1 h is nonuniform,

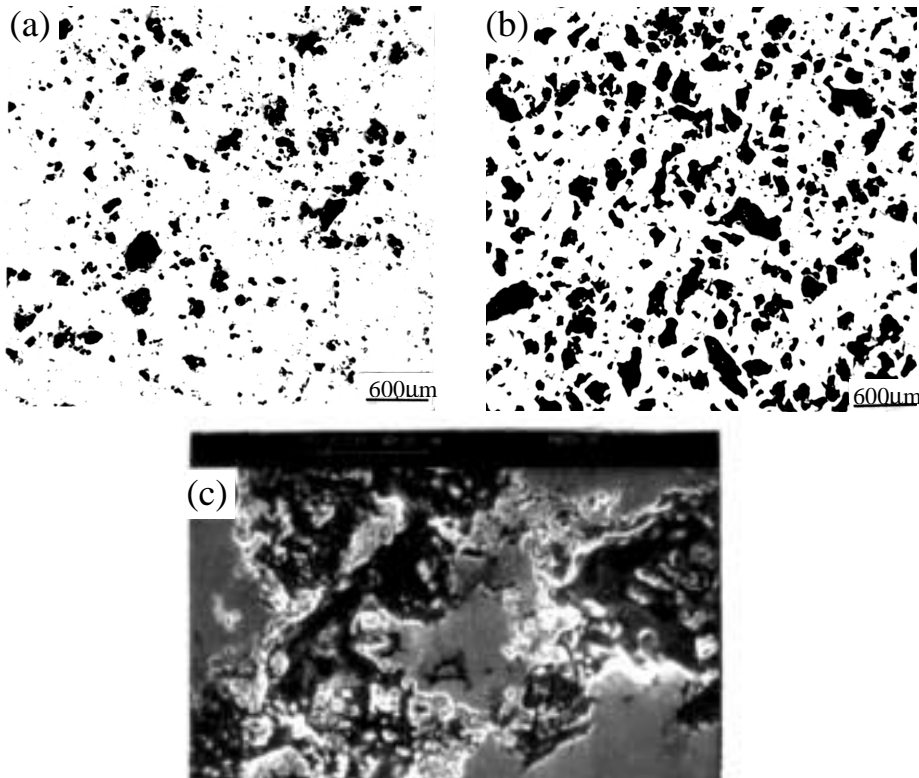


Fig. 2. The microstructure of porous NiTi alloy. (a) 1023K-1h; (b) 1223K-9h; (c) 1223K-3h.

which is related to the incomplete sintering degree. While the pore size and distribution of porous alloy

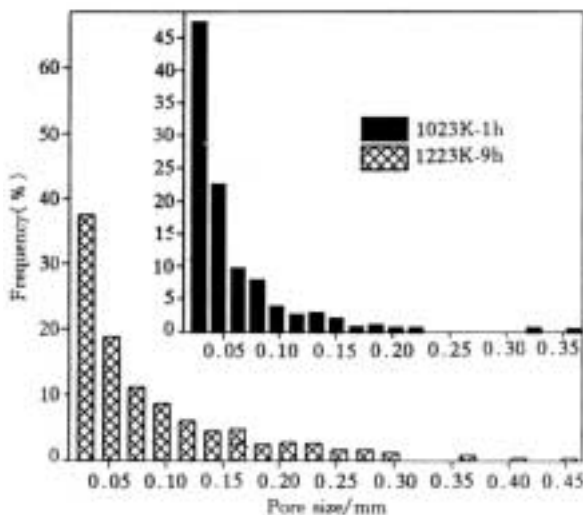


Fig. 3. Pore size distribution of porous NiTi alloy.

sintered at 1223 K-9 h is very uniform and the pore edges are clean, which both show that at 1223 K-9 h the sintering reaction is complete and the sintering product has good sintering properties. The corresponding average pore size obtained by means of image analysis are 52.6 μm and 82.8 μm , respectively. The pore size distribution of porous NiTi alloy is shown in Fig. 3. As can be seen, the pore size smaller than 50 μm of alloys sintered at 1023 K-1 h is over 70% while that of 1223 K-9 h is less than 45%. The increase of average pore size after sintered at 1223 K-9 h and the homogenization of pore size and its distribution are due to the increase of sintering temperature and sintering time,

which enhance the interdiffusion between Ti and Ni, and the enhancement of sintering degree makes the smaller pores shrinkage and even vanish, thus the average pore size increases after sintered at 1223 K-9 h. The pore morphology sintered at 1223 K-3 h is shown in Fig. 2c. The inner matrix is sponge-like and interconnected, which further demonstrates the good interconnection of pores.

2.3 X-ray analysis

XRD patterns for samples before sintering and after sintering are shown in Fig. 4. Since only pure Ni and pure Ti are existed in blended powders and no intermetallic is found, the Ni and Ti powders are just mechanically blended and no chemical reaction occurs. After sintered at 1023 K-1 h or 1223 K-9 h, B2 (NiTi), B19' (NiTi), Ti₂Ni and Ni₃Ti are presented. But there is a small amount of pure Ni and pure Ti after sintered at 1023 K-1 h, in which Ni₃Ti is the dominant phase. In contrast, no pure Ni is found in porous NiTi alloys after sintered at 1223 K-9 h, in which B2 (NiTi) is the dominant phase. The sintering process at 1223 K-9 h is complete as NiTi, Ti₂Ni and Ni₃Ti are stable phases. Since pure Ni is carcinogenic, that no pure Ni is found in the XRD pattern of alloy sintered at 1223K-9h is just as expected in present study.

Compared with the alloy sintered at 1023 K-1 h, after sintered at 1223 K-9 h the NiTi phase is obviously increased while Ni₃Ti and Ti₂Ni are decreased. This can be attributed to the high sintering temperature, which enhances the diffusion rate and makes the reaction tend to equilibrium [6].

2.4 Superelasticity of porous NiTi alloy

As one of the promising medical implants and devices, present NiTi alloy not only has porous structure, but also has excellent SME and SE. The SE of porous NiTi alloy is shown in Fig. 5. As can be seen, the elastic deformation, 6.0~7.5%, is far much higher than the "Hook" elastic deformation of ordinary metallic materials. The elastic deformation increases greatly with increasing sintering temperature at the range of 1023 K ~1223 K, and the elastic deformation of alloy sintered at 1223 K-9 h is the highest. Moreover, after prestrain 30% the elastic deformation of alloy sintered at 1223 K-1 h can reach 12.6%, which excels that of bulk NiTi alloy. Therefore, present porous NiTi alloy has good SE, which is associated with the deformation mechanism of NiTi alloy. Under applied load, the martensite is induced by applied stress, i.e., the B2 parent phase transforms into martensite. This stress-induced-martensite goes an inverse transformation into the B2 parent phase during unloading. Thus NiTi alloy exhibits SE. In addition, the deformation of porous NiTi alloy has its own characteristics. The matrix pore wall is thin for the existence of large amount of pores, which can be easily deformed. When the deformation of pore walls (the matrix) reaches 8%, the elastic deformation limit of bulk NiTi alloys, the deformation of the whole porous material is very higher than 8%. During the followed unloading, the pores tend to recover their original shape and

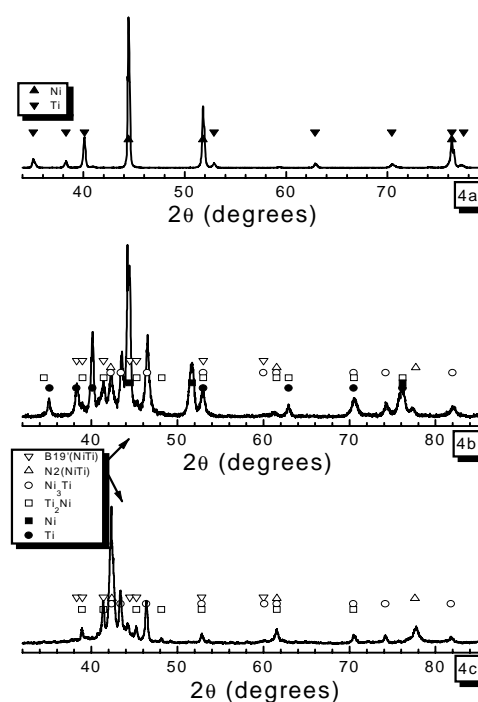


Fig. 4. (a) XRD patterns of samples before sintering. (b) XRD patterns of samples after sintering at 1023 K-1 h. (c) XRD patterns of samples after sintering at 1223 K-9 h.

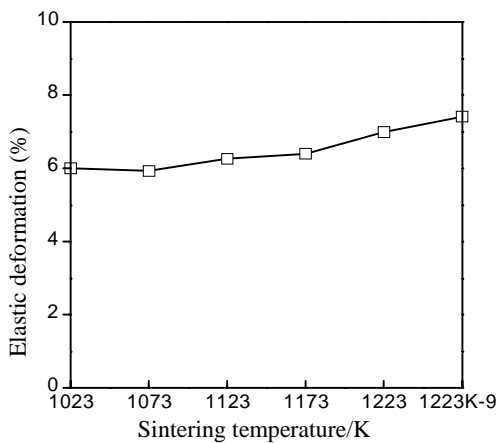


Fig. 5. Superelasticity of porous NiTi alloy ($\epsilon_i=8\%$).

size accompanied with the shape recovery of the matrix. As a result, porous NiTi alloy has better SE than bulk alloy. However, the deformation of porous alloy is nonuniform, there appear regions of the matrix where the strain exceeds the recoverable strain limit (8%). Therefore, porous NiTi alloy can not recover its shape completely by heating higher than the martensitic transformation point.

2.5 Comparison with the biomedical requirements

Compared with the biomedical requirement of porous NiTi materials [7,8] (Table 1), the experimental porous NiTi alloy satisfies these requirements to a great degree. A key step has been made in the research and application of porous NiTi alloy, which provides the basis for further research in this field. Although the sintered porosity is relatively low and the pore size is a little small, the SE and strength of porous NiTi alloy are excellent and can satisfy the biomedical requirement for choice of implanting materials in medicine.

Table 1 The comparison of experimental results with the biomedical requirement of porous NiTi alloy

	Refs. [7, 8]	Experimental
Porosity / %	30—90	36.0—41.5
Interconnectability of pores	interconnected	>96% is interconnected
Pore size/ μm	bone tissue:100—500 connective fibrous tissue:<100	<100
Pure Ni	not allowed	1023 K-1 h existed 1223 K-9 h is not found by XRD
Strength limit/ MPa	200~1000 ^{a)}	>150 ^{b)}

a) Normally, the tensile and compaction strength of bone are 130 and 150 MPa, respectively. b) The stress at strain of 8% during compaction.

3 Conclusions

1) Porous NiTi alloys with pore size smaller than 100 μm and porosity in the range 36.0~41.5% have been obtained by elemental powder sintering. The pores are almost interconnected, and the open pore-ratio is higher than 96%. The pore size and pore distribution of alloy sintered at 1223 K-9 h are homogeneous.

2) Porous NiTi alloys with different phase composition can be achieved by controlling the sintering conditions. There is a small amount of pure Ni and Ti in alloy sintered at 1023 K-1 h, while no pure Ni is found by XRD after sintered at 1223 K-9 h.

3) Porous NiTi alloy has better SE than that of bulk alloy due to the existence of pores. The elastic deformation of alloys sintered at 1223 K-9 h reaches up to 7.4% at prestrain of 8% and more than 12% at a large prestrain.

4) It is applicable to obtain porous NiTi alloy by powder metallurgy technique. By comparison, porous NiTi alloy sintered at 1223 K-9 h satisfies the biomedical requirement for choice of implant materials to a great degree.

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