Vol. 42 No. 1 SCIENCE IN CHINA (Series E) February 1999

Microstructure and superelasticity of porous NiTi alloy*

LI Bingyun (李丙运), RONG Lijian (戎利建) and LI Yiyi (李依依)
(Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Chinese Academy of Sciences,
Shenyang 110015, China)

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 1 223 K-9 h. Compared with the biomedical criteria for choice of implanting materials, porous NiTi alloy is satisfying to a great degree.

Keywords: powder sintering, porous alloy, NiTi shape memory alloy, superelasticity.

The mechanical deformation behavior of biological materials, of 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[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 good quality 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 material, 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, "863" Committee for High Technique and Committee for

---

* Project supported by the Chinese Academy of Sciences under key program (Grant No. 971524).

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 up 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 sintering conditions are as follows: (i) sintered for 1 h at different temperatures; 1 023, 1 073, 1 123, 1 173, 1 223 K; (ii) sintered at 1 223 K for different times: 1, 3, 5, 7, 9 h. It is found[3] that 1 223 K-9 h is the optimal sintering condition and thus we focus mainly on porous NiTi alloy sintered at 1 223 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 a DCS-10t Instron testing machine. The porosity and open pore-ratio were determined as the method used in references [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. 1(a) 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 in accordance with ordinary sintering densification process. Moreover, the linear decrease of sintered porosity with increasing sintering temperatures in the range of 1 023—1 173 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 satisfies this biomedical requirement. Also, the open pore-ratio

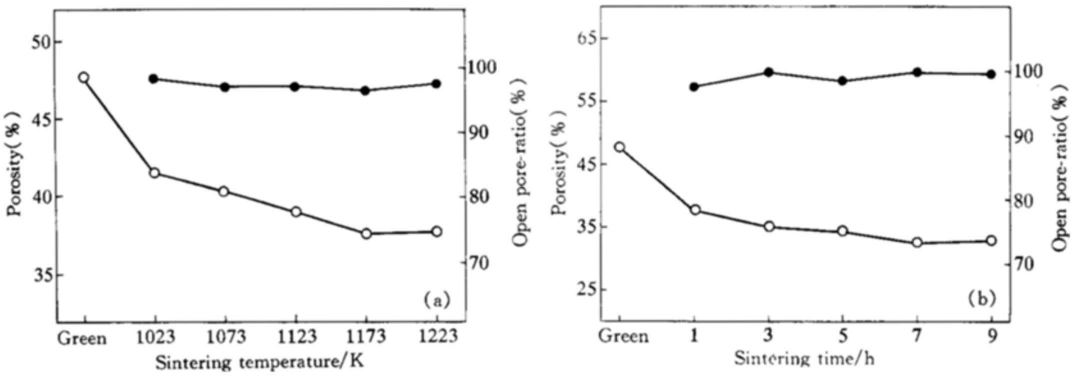

Fig. 1. (a) Dependence of porosity and open pore-ratio on sintering temperature. (b) Dependence of porosity and open pore-ratio on sintering time at 1 223 K. ○, Porosity; ●, open pore-ratio.

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

2.2 Pore size, morphology and distribution

Shown in fig. 2(a) and (b) are micrographs of porous NiTi alloys sintered at 1 023 K-1 h and 1 223 K-9 h, respectively. One can see that the pore size of porous NiTi alloy sintered at 1 023 K-1 h is nonuniform, which is related to the incomplete sintering degree, while the pore size and distribution of porous alloy sintered at 1 223 K-9 h is very uniform and the pore edges are clean, which both show that at 1 223 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 is 52.6 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 1 023K-1 h is over 70% while that of 1 223 K-9 h is less than 45%. The increase of average pore size

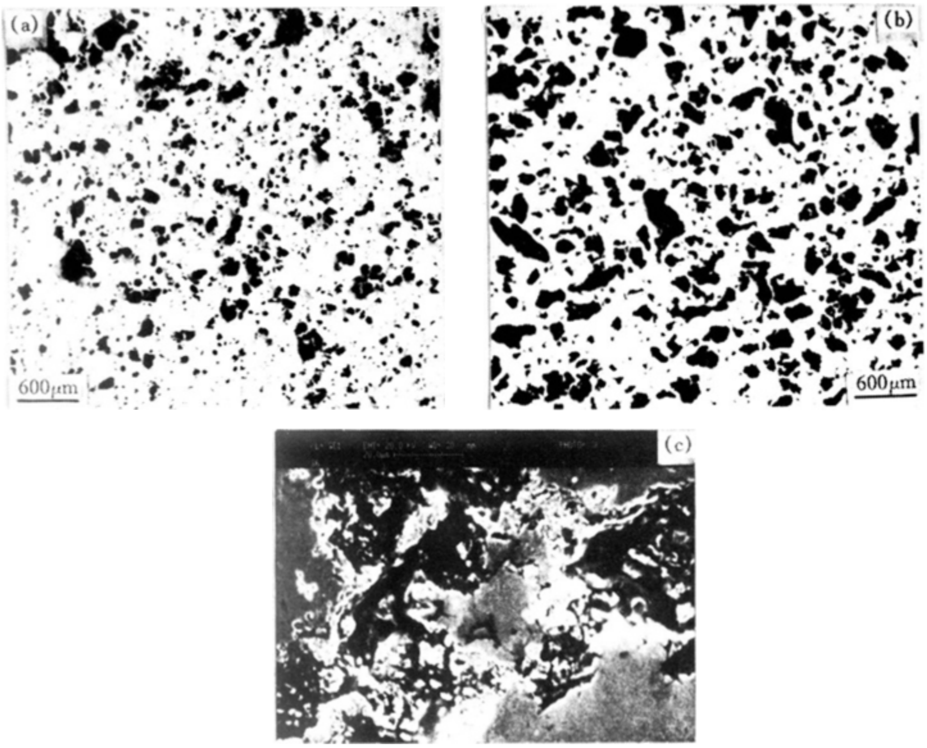

Fig. 2. The microstructure of porous NiTi alloy. (a) 1 023K-1 h; (b) 1 223 K-9 h; (c) 1 223 K-3 h.

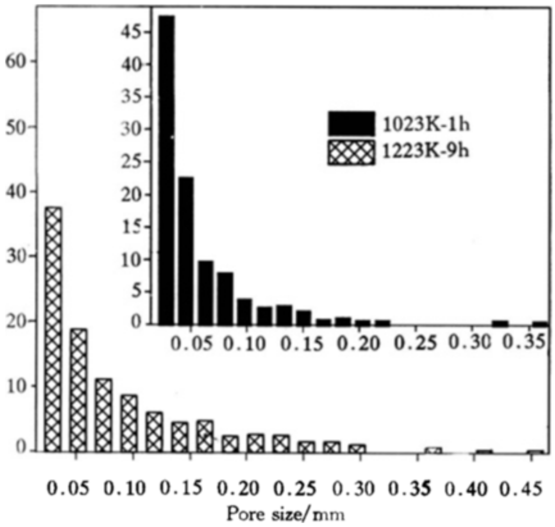

Fig. 3. Pore size distribution of porous NiTi alloy.

after sintered at 1 223 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 shrink and even vanish. Thus the average pore size increases after sintered at 1 223 K-9 h.

The pore morphology sintered at 1 223 K-3 h is shown in fig. 2(c). 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 exist in blended powders and no intermetallic compound is found, the Ni and Ti powders are just mechanically blended and no chemical reaction occurs. After sintered at 1 023 K-1 h or 1 223 K-9 h, B2 (NiTi), B19′ (NiTi), Ti_2Ni and Ni_3Ti are presented. But there is a small amount of pure Ni and pure Ti after sintered at 1 023 K-1 h, in which Ni_3Ti is the dominant phase. In contrast, no pure Ni is found in porous NiTi alloys after sintered at 1 223 K-9 h, in which B2 (NiTi) is the dominant phase. The sintering process at 1 223 K-9 h is complete as NiTi, Ti_2Ni and Ni_3Ti are stable phases. Since pure Ni is carcinogenic, that no pure Ni is found in the XRD pattern of alloy sintered at 1 223 K-9 h is just as expected in the present study.

Compared with the alloy sintered at 1 023 K-1 h, after sintered at 1 223 K-9 h the NiTi phase is obviously increased while Ni_3Ti and Ti_2Ni are decreased. This can be attributed to the high sintering temperature, which enhances the diffusion rate and makes the reaction tend to equilibrium[6].

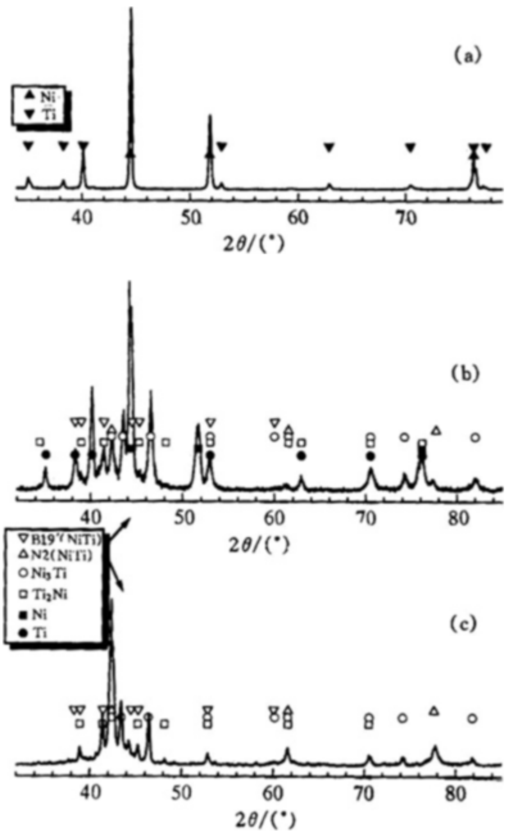

Fig. 4. (a) XRD patterns of samples before sintering. (b) XRD patterns of samples after sintering at 1 023 K-1 h. (c) XRD patterns of samples after sintering at 1 223 K-9 h.

2.4 Superelasticity of porous NiTi alloy

As one of the promising medical implants and devices, the 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 much higher than the "Hook" elastic deformation of ordinary metallic materials. The elastic deformation increases greatly with increasing sintering temperature in the range of 1 023—1 223 K, and the elastic deformation of alloy sintered at 1 223 K-9 h is the highest. Moreover, after 30% prestrain the elastic deformation of alloy sintered at 1 223 K-1 h can reach 12.6%, which excels that of bulk NiTi alloy. Therefore, the present porous NiTi alloy has good SE, which is associated with the deformation mechanism of NiTi alloy. Under applied load, the matensite is induced by applied stress, i.e. the

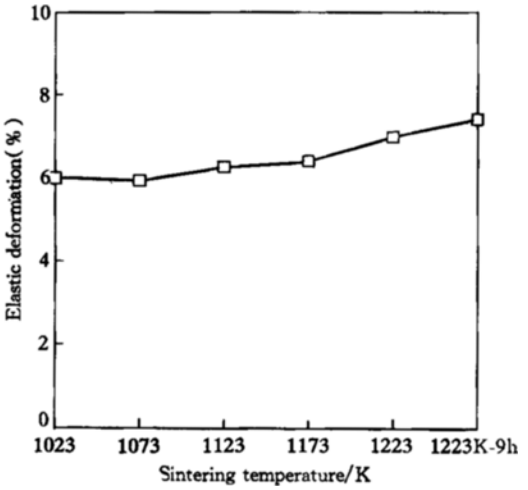

Fig. 5. Superelasticity of porous NiTi alloy ($\varepsilon_t = 8\%$).

B2 parent phase transforms into martensite. This stress-induced-martensite experiences 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 higher than 8%. During the following unloading, the pores tend to recover their original shape and size accompanied by 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 cannot recover its shape completely by heating higher than the martensitic transformation point.

2.5 Comparison with the biomedical requirements

Compared with the biomedical requirements 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 requirements 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	1 023 K-1 h existed 1 223 K-9 h is not found by XRD
Strength limit/MPa	200—1 000[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 of 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 1 223 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 1 023 K-1 h, while no pure Ni is found by XRD after sintered at 1 223K-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 1 223 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 1 223 K-9 h satisfies the biomedical requirements for choice of implanting materials to a great degree.

References

1 Gyunter, V. E., Sysoliatin, P., Temerkhamor, T. et al., *Superelastic Shape Memory Implants in Maxillofacial Surgery, Traumatology, Orthopaedics, and Neurosurgery*, Tomsk: Tomsk University Publishing House, 1995, 14.

2 Martynov, I., Skorohod, V., Solonin, S. et al., Shape memory and superelasticity behavior of porous Ti-Ni material, *J. de physique*, 1991, 4(1): 421.

3 Li Bingyun, Rong Lijian, Li Yiyi, Porous NiTi alloy prepared from elemental powder sintering, To be published in *J. Mater. Res.*

4 Yao Dechao, *Experimental Technique in Powder Metallurgy* (in Chinese), Changsha: Metallurgical Industry Publishing House, 1990, 15.

5 Users manual of the density determinator of Satorius YDK01, 1995.

6 Hey, J. C., Jardine, A. P., Shape memory TiNi synthesis from elemental powders, *Mater. Sci. Eng.*, 1994, A188: 291.

7 Itin, V. I., Gyunter, V. E., Shabalovskaya, S. A. et al., Mechanical properties and shape memory of porous nitinol, *Mater. Character*, 1994, 32: 179.

8 Gyunter, V. E., Itin, V. I., Monasevich, L. A. et al., *Shape Memory Effects and Their Application in Medicine*, Novosibirsk: Nauka, 1992.