Advanced Materials Research Vol. 1085 (2015) pp 430-435
© (2015) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMR.1085.430

Submitted: 07.07.2014
Revised: 24.08.2014
Accepted: 13.10.2014

Study of Structural Features of Porous TINI-based Materials Produced by SHS and Sintering

ANIKEEV Sergey G.[a], KHODORENKO Valentina N.[b], KOKOREV Oleg V.[c], CHEKALKIN Timofey L.[d], GUNTER Victor E.[e]

Tomsk State University, 36, Lenina street, Tomsk, 634050, Russia

[a]Anikeev_sergey@mail.ru, [b] Hodor_val@mail.ru, [c] Kokorevov@yandex.ru, [d] Tc77@mail2000.ru, [e]Tc77@rec.tsu.ru

Keywords: Nitinol, TiNi, porous, self-propagating high-temperature synthesis (SHS), diffusion sintering, structure, strength and deformation properties.

Abstract. Structural properties of porous TiNi-based materials produced by SHS method and sintering have been investigated. The material having different pore wall surface topography, porosity and pore size distribution was shown to be produced depending on the powder metallurgy method for porous TiNi-based alloy. All the materials having porosity of 55-70%, mean pore size 90-150 μm, as well as normal pore size distribution are most preferable. Ultimate strength and breaking point were determined to depend on porosity, pore size distribution, pore intersections and phase-chemical composition of the material. Strength properties of the sintered alloy are twice as much compared to the SHS-produced ones due to homogeneity of its macrostructure, low chemical heterogeneity and $TiNi_3$ precipitations strengthening the TiNi matrix.

Introduction

Porous TiNi-based materials are very popular in medicine and technical applications. Effective use of them is associated with the unique properties of these materials. The material is capable to show highly elastic properties similar to those of body tissues and to change their shape under temperature and stress influence. It also has porous structure, and due to open pores it's occurred to be specific thermally-stable system having high wettability by tissue fluids and high degree of biomechanical and biochemical compatibility at the cellular level [1-9].

The porous structure and the pore space in TiNi-alloys play a significant functional role because when applying the material inside a human body it is filled with tissue fluids and living tissues. Porous metallic matrix gets into complex interaction with body tissues, including mechanical, electrochemical, thermal, hydrodynamic and other forms of interaction. Beside that strength properties of porous TiNi-based alloy depend on its structural properties — porosity, pore size distribution and pore intersections, structural and phase composition.

Structural and strength properties are determined by the method of production. Porous TiNi-based alloys can be produced by powder metallurgy methods: self-propagating high-temperature synthesis (SHS) from Ni and Ti powders, as well as by diffusion sintering of TiNi-powder [10, 11].

SHS method allows producing of porous materials with high porosity, specific pore size distribution and pore walls morphological characteristics. Porous materials produced by sintering of TiNi-powder are characterized by the properties similar to those which are exhibited by the SHS-produced materials. However, the main difference between them as follows: size factor, surface topography of the pore walls and phase and chemical composition of the metal matrix. A decent number of works are devoted to studying of porous materials. However, these articles don't contain sufficient comparative data on physical and mechanical properties of sintered and SHS-produced porous materials.

In this regard, an important and vital aim in this field is to be a comprehensive studying of matrix properties of porous TiNi-materials, as well as studying of pore space condition and physical and mechanical properties of the materials produced by different methods.

The purposes of this work are to study the structural properties of matrix and pore space in TiNi-based alloys and determine strength and deformation characteristics of the materials produced by SHS and sintering methods.

Materials and methods

Samples of porous TiNi-based materials were produced by two methods — SHS method and diffusion sintering. For SHS method the following grades of materials were used: Ti powder PTM, PTOM and Ni powder PNK-10T2, PNK – 1L5 (Russian brand/classification). Sample charges were obtained at the initial synthesis temperature 400^0C and 600^0C. From these charges the samples were then ED cut off the rectangular pieces having the following sizes 3.5×3.5×31 mm.

The samples obtained by the method of double sintering were produced from Titanium powder PN55T45S (Russian brand/classification). To get the samples small in shape and to avoid the reaction with hydrogen contained in molds the first sintering was performed at 1200°C for 40 min. The second sintering was carried out in temperature range from 1220 to 1260°C for 40 min. The most appropriate material in terms of its structural and strength properties was then selected for studying. This material was obtained at 1250^0C of second sintering; diameter 3.5 mm, length 30 mm.

In order to study macro- and microstructure of the samples prepared thin sections were obtained by means of standard technique. Metallographic examination was carried out using optical microscope Axiovert-40 MAT. Microstructure analysis, phase analysis and topographical studies of pore wall surface were SEM carried out using Philips SEM 515 and Quanta 200 3D.

A quantitative description of the pore structure was performed. Porosity was determined by weighing technique. The size of pores and pore intersections was determined by combination of the secant method and the method of inscribed spheres.

Strength properties of porous alloys (ultimate strength, strain to fracture) were performed using bending test because its deformation mechanism in the samples is confirmed to be most closely correspondent to actual operation conditions of implants in human body.

Results and discussion

It was determined that the main matrix component of samples obtained in both SHS method and sintering method is a complex intermetallic composition TiNi(MoFe), represented by two phases B2 and B19′ (Fig. 1 a, b). Precipitations Ti_2Ni and $TiNi_3$ are contained in the samples in significant amount, and these phases are distributed heterogeneously in the matrix phase (Fig. 1 a). Areas of these precipitations are usually located along pore boundaries and along grain boundaries as well. Phases enriched with Ti_2Ni are occured to be non-coherent and represented by fine particles, preferably round- or platelet-shaped and more rarely grid-shaped.

Porous SHS materials are characterized by significant heterogeneity of secondary phase distribution compared to sintered materials due to special features of SHS method [3]. The main specific characteristic of sintered porous material is Ni-enriched matrix due to escaping of Ti-atoms from melted phase Ti_2Ni during sintering. This process contributes to enrichment of matrix with fine $TiNi_3$ precipitations, which significantly affect the strain-strength properties of the alloy.

Macrostructure of porous-permeable NiTi-alloy obtained in SHS and sintering methods represents the 3D pore cluster which morphological structure is typical to highly porous materials obtained through the eutectic reaction. Porous materials have a large specific surface due to open and interconnected pores. Using a variety of production methods, changing the temperature and time modes, properties of the green powders one can obtain different porous-permeable materials with distinguished structure and features. Depending on these parameters the materials produced can have different minimum and maximum pore size, pore size distribution as well as, most importantly, different surface condition of pore space surface — topography of pore walls, phase structure, chemical composition. Samples of SHS-produced materials have porosity of 75%, disordered porous structure with pore size in the range of 0.1-1000 µm and the mean pore size of 150 µm (Fig. 2 a).

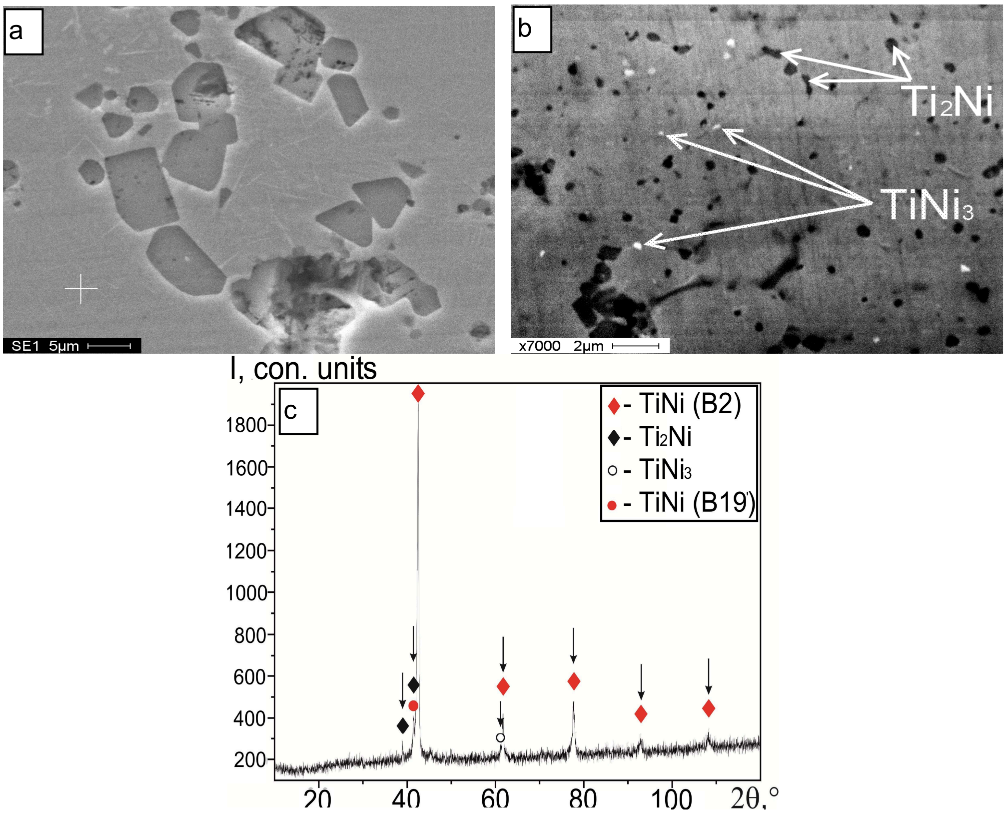

Fig. 1. Microstructure of porous TiNi-based alloy produced by sintering (a) and SHS (b); X-ray diffraction pattern of the porous matrix (c)

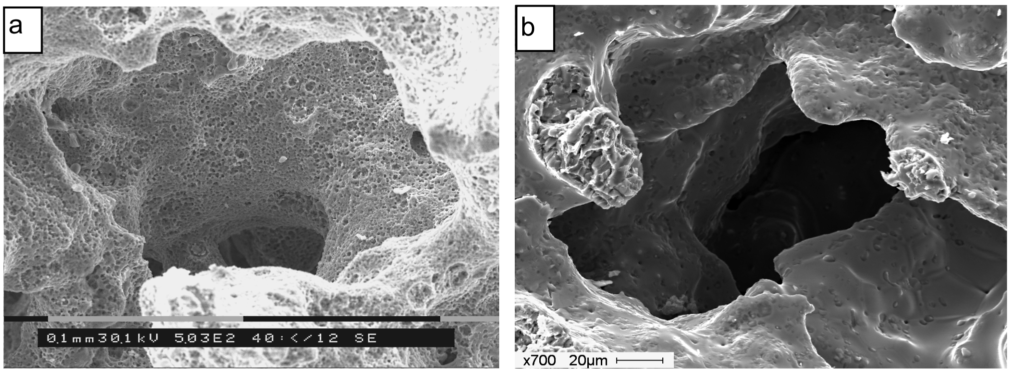

Fig. 2. Structure of porous TiNi-based alloys produced by SHS (a) and sintering (b)

Depending on the SHS modes, porous materials with micro- and nano-sized pores can be produced. Studies made using mercury injection technique for measuring of pore size have shown that nano-sized pores, 1-100 nm, are also found in the alloy along with open pores [12].

Sintering method allows obtaining of fine-porus materials having pore size in the range from 2 to 375 µm. The porosity is 55%, the mean pore size is 90 µm. Histograms of pore size distribution for SHS-produced and sintered materials are shown at Fig. 3. Both cases the pore size distribution has a single-mode character. However, the histogram of SHS-produced material unlike that of sintered material has a wider range of pore sizes: apart from nano- and micro-sized pores the pores of larger sizes, from 300 to 1000 µm are also represented. The structural characteristics of sintered material are such that histogram is limited by pore sizes up to 350 µm and nano-pore aren't virtually observed.

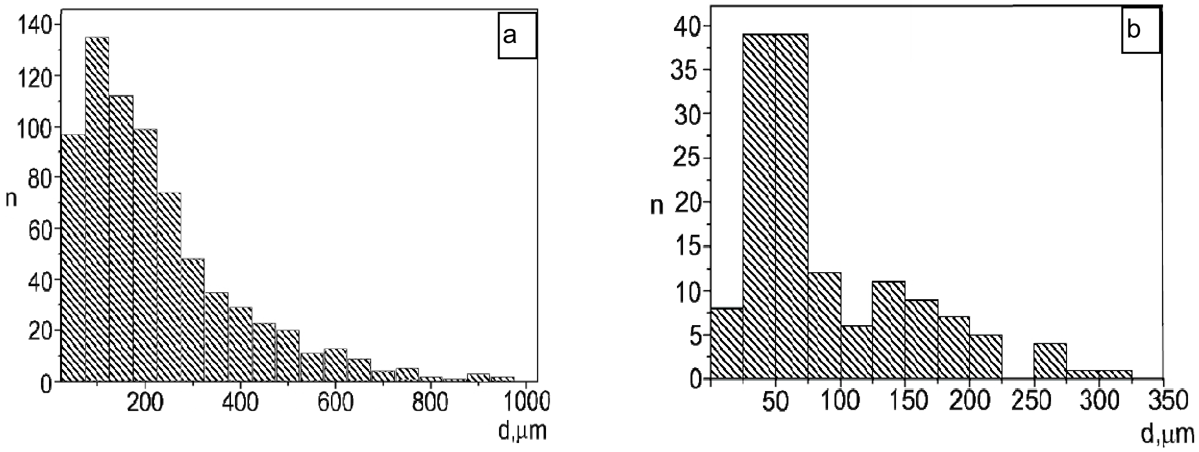

Fig. 3. Histograms of pore size distribution for SHS (a) and sintered (b) samples

The mean size of pore intersections in both materials is 127 μm. However, in sintered material the amount of pore intersections which have similar dimensions is substantially greater than in SHS-produced material. Thus, in sintered material due to the absence of large pores and greater amount of pore intersections which have similar dimensions, the macrostructure of pore space is more homogeneous than that of SHS-produced material. This macrostructural feature of porous materials significantly affects their physical and mechanical properties.

Porous materials obtained by different methods, are different in fine structure of pore walls (see Fig. 2). The surface of pore walls in the SHS-produced material is well-developed, well-shaped, rough and micro-porous, and contains a large number of micro- and nano-pores (Fig. 2a). In sintered material pore walls are smoother and contain a less number of small pores (Fig. 2b). Pore space formation which is characterized by fine structure of pore walls and specific phase and chemical composition of the matrix is governed by technological characteristics of the methods of porous materials production — different temperatures and times of the process, synthesis and sintering reaction rates, type of powders, etc.

Structural characteristics play an important role in selection of material required for specific medical goals. Pore walls surface topology, pore size distribution, porosity are the main properties in choosing a porous material.

Table 1 shows the physical and mechanical properties of SHS-produced and sintered materials obtained in bending test. It can be easily seen that ultimate strength of sintered material is almost twice as much compared to SHS one. As noted, the SHS samples differ by strongly marked phase and chemical heterogeneity as well as heterogeneous macrostructure. The maximum stress during fracture can be attained at the condition of similar size of pores and pore intersections [13].

Table 1. Strength properties of porous TiNi-based materials produced by SHS and sintering methods

Material	Porosity, %	Mean pore size, μm	Ultimate strength, MPa	Fracture strain, %
SHS	75	150	38	10
Sintering	55	90	75	5

High ultimate strength of sintered material is due to several factors: macrostructure homogeneity and less pronounced phase and chemical heterogeneity, as well as by the presence in matrix of strengthening $TiNi_3$ precipitations. Sintering process occurs due to appearing of liquid phase Ti_2Ni, that changes the concentration of Ti and Ni in the matrix by reducing Ti-content and increasing Ni-content. Apart from that, during sintering process Ti atoms are segregated at newly-formed free surfaces with formation of the oxide layer [14, 15]. This leads to deviation from stoichiometric ratio of the TiNi matrix by Ni enriching, as a consequence, the process of $TiNi_3$ fine precipitations occurs. These precipitations get the matrix strengthened significantly while reducing the amount of plastic deformation. That's why the fracture strain of sintered material is lower comparing to the SHS-material. When the macrostructure of sintered material is homogenous and the sizes of pore intersections are equal the stress applied is distributed uniformly between all monolithic pore intersections and the entire material is deformed integrally, that enhances the strength properties significantly. In case of heterogeneous structure, when both small and large pore intersections are represented in the material, under condition of isostatical loading the cracks originate from the pore intersections which fail to withstand a certain strain. When loading increases they will break first. Redistribution of stress results in additional loading of undamaged pore intersections. It's to be noted that in work [16] the significant increase of strength properties of porous TiNi-based alloy was attained by Al doping also due to homogenous macrostructure formation and dispersed solidifying of the TiNi phase. Thus, ultimate strength and breaking point for sintered and SHS materials are considerably determined by the particular characteristics of their macro- and microstructure.

Fracture surfaces analysis of porous materials has shown that their fracture behavior is virtually identical. All samples are characterized by the ductile-brittle fracture. The signs of cup fracture and ductile-brittle fracture along the boundaries of martensite platelet-shaped crystals of phase B19′ are represented in the material. It is important to underline that the fracture behavior depends on the size factor of pore intersections. In large pore intersections the both types of fracture are observed and appear gradually and locally due to heterogeneous matrix composition. Small pore intersections were turned out to show preferably cup fracture topology with thin pore walls. Fractograph patterns adequately reflect the structural characteristics of both porous materials.

Conclusion

Studies have shown that porous TiNi-based materials produced by different methods, are characterized by distinguished structural properties. SHS material has heterogeneous macrostructure of pore space with well-developed microstructure of the pore wall surface, a wide range of pore and pore intersection sizes and heterogeneous phase and chemical composition of the matrix. Sintered material differs by more homogeneous microstructure of the matrix, doesn't contain large pores and has similar in size pore intersection. The structure of materials investigated is responsible for their mechanical properties. It was also found that increasing of the strength properties of sintered material occurs due to the homogeneity of its macrostructure, less pronounced phase and chemical heterogeneity and strengthening of the matrix with $TiNi_3$ precipitations. Physical and mechanical characteristics of both materials (ultimate strength, breaking point) – are met the technical requirements for the materials used in wide clinical practice.

Acknowledgments

The authors gratefully acknowledge the support for this research provided by the Tomsk State University Competitiveness Improvement Program. This support is greatly appreciated.

References

[1] V.E. Gunter, Shape memory materials and new technologies in medicine, NPP «MIC», Tomsk, 2010.

[2] V.E. Gunter, Shape memory materials and new technologies in medicine, NPP «MIC», Tomsk, 2007.

[3] V.E. Gunter, V.N. Khodorenko, T.L. Chekalkin, Medical materials with shape memory, Medical materials and shape memory implants, first ed., NPP «MIC», Tomsk, 2011.

[4] V.E. Gunter, Biocompatible materials with shape memory and new technologies in dentistry, NPP «MIC», Tomsk, 2006.

[5] V.N. Khodorenko, A.V. Gunter, A.A.Radkevich, Biocompatibility of fine-grained porous NiTi with biological tissues, Shape memory materials and new technologies in medicine, 2004.

[6] O.V. Kokorev, V.N. Khodorenko, S.G. Anikeev, Study of the behavior of mesenchymal stem cells in the bone marrow of porous permeable incubators of NiTi, NTL, Herald of New Med. Technol. 19,1 (2012) 32-36.

[7] O.V. Kokorev, V.N. Khodorenko, G.Z. Dambaev, Comprehensive assessment of the development of hepatocytes in the porous-permeable incubators of NiTi, Siberian J. of Medicine. 27,1 (2012) 130-36.

[8] O.V. Kokorev, G.Z. Dambaev, V.N. Khodorenko, V.E. Gunter, Porous-permeable incubators of NiTi in cell technologies, Cellular Transplantology and Tissue Eng.1-2 (2010) 68-76

[9] K. Otsuka, X. Ren, Physical metallurgy of Ti–Ni-based shape memory alloys, Progress in Materials Science (2005)

[10] V.I. Itin, Y.S. Naiborodenko, High-temperature synthesis of intermetallic compounds, TSU, Tomsk, 1989.

[11] A.P. Savickii, Liquid-phase sintering systems with interacting component, Science Siberian Branch, Novosibirsk, 1991.

[12] Y.F. Yasenchuk, V.N. Khodorenko, V.E. Gunter: Segregation of titanium during heat treatment of porous NiTi, Shape memory materials and new technologies in medicine (2004).

[13] V.E. Gunter, Metallography in medicine and especially the deformation behavior of materials and implants superelastic shape memory, Implants with Shape Memory. 1-2 (2012) 98-110.

[14] S.P. Belyaev, F.Z. Gilmutdinov, O.M. Komunnikova, Investigation of the processes of oxidation and segregation on the surface of NiTi, Letters to Technical Physics Letters. 25-13 (1999) 84-89.

[15] U.F. Yasenchuk, V.N. Khodorenko, V.E. Gunter, Segregation in the heat treatment of titanium porous NiTi, Implants with Shape Memory.1-2 (2005) 14-18.

[16] A.N. Monogenov, N.V. Artyuhova, Y.F. Yasenchuk, Mechanical properties of porous NiTi aluminum-doped, Fund. Problems of Modern Mater. 63 (2009) 59-64.