Conference paper

A Study of the Pore Surface State of Porous TiNi-based Materials Obtained by SHS at Various Ignition Temperatures

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Abstract

Structural features of porous TiNi-based materials obtained by SHS at temperatures of synthesis beginning of 400 °C and 600 °C have been investigated. It is found that finely porous material with a porosity P=75 % was obtained at the temperature of 400 °C. A surface of pore walls contains a dendritic relief, oxycarbidenitride layer and a multitude of secondary phase particles. Phase and chemical composition of the material is non-uniform. SHS material obtained at the synthesis beginning temperature of 600 °C is characterized as a coarse-porosity one P=65 %. Nano- and micropores are practically absent. The oxycarbidenitride surface layer with a variable thickness is substantially free of secondary inclusions due to the more complete processes of alloy formation. This layer has an own substructure based on carbonitride and oxynitride layers.

1 Introduction

Using the method of self-propagating high-temperature synthesis (SHS) allows to create porous-permeable medical materials with controllable characteristics of the structure and physico-mechanical properties [1]. SHS method is based on the use of an internal chemical energy of initial components of powder application phase. From the energy point of view it provides the most efficient production of porous materials.

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The process of TiNi alloy producing in the SHS wake is entirely adjusts with the TiNi diagram. The maximum temperature of the powder composition combustion coincides with liquidus temperatures of the TiNi diagram state [2]. Upon reaching liquidus temperature during synthesis the components are completely dissolved in the eutectic melt. After an exothermic reaction of Ti and Ni powder an interaction product is a liquid solution, a crystallized phase is an intermetallic compound. Temperature heterogeneity in the combustion front is a consequence of the non-uniform distribution of elements concentration in the melt, which exists for a short time. Redistribution of components between the crystallized liquid solution and the solid phase is carried out in the process of non-equilibrium crystallization. The intermetallic compound composition corresponds to a composition of the original powder composition. A presence of other phases is connecred with a purity of starting powders and phase separation processes during crystallization [2].

The synthesis process depends on several parameters: a pressure in the reactor [3], thermal vacuum treatment (drying) of powders, the mutual ratio of powder component, various chemical alloying elements [1, 2]. However, the most important adjustable parameters of the synthesis process are an initial size and porosity of the preform, a granulometric composition and dispersion of the powder composition, the temperature of the synthesis beginning [1].

Temperature conditions of synthesis have a fundamental importance in preparation of a porous material with desired characteristics. Heat distribution in the sintered powder system determines the combustion mode. Burning rate increases with increasing initial temperature [1]. Changing the initial heating temperature with following changing the ratio of temperatures in the synthesis wave can affect the morphology and phase composition of the final product [2].

Influence features of temperature modes of combustion on properties of SHS materials are presented in works [4]. It was found that at beginning synthesis temperatures of 250-300 °C obtaining porous TiNi based alloy passes in pulsed mode of layerwise combustion, and at temperatures of 400–600 °C it occurs in continuous mode. Therefore, in this study the SHS materials were received at synthesis beginning temperatures of 400 °C and 600 °C, as it allows creating a porous material with a higher degree of uniformity than at lower temperatures.

A surface state of the pore walls is important in prospects for using SHS material in a medical practice, as body cells come into close interaction with the implant and seek to consolidate of the pore walls on the surface. The integration processes of the implant into the body depend on a biochemical and biomechanical reaction at first in a cellular level, and then in a tissue level. A presence of micropores and a high degree of roughness improve adhesion properties of the surface. It accelerates integration processes of cell cultures in the implant. Therefore, a comprehensive study of structural features and the surface state of pore walls for porous-permeable materials obtained by SHS at different temperatures of synthesis beginning of 400 °C and 600 °C are highly relevant research.

2 Experimental

The porous TiNi-based alloy by SHS was obtained from titanium powders PTOM and nickel powders PNK-1L5. The powders were dried in a laboratory vacuum oven for 4-8 hrs. The powder charge was filled in quartz tube and compacted for 30 minutes. Next, the quartz tube with the charge was set in the reactor and was heated in a tubular electric furnace in an inert gas atmosphere. It was found that at temperatures of the synthesis beginning of T=400 °C and T=600 °C different structural states of materials were formed due to peculiarities of a passage of the combustion wave. The high-temperature synthesis was initiated by short-circuiting an electric circuit. After passing the combustion wave the reactor with obtained alloy was cooled in water, then porous TiNi alloy was removed from the quartz tube. From obtained cylindrical billets the samples was cut out on the electric spark machine for further research. A macro- and microstructure of samples was studied by means of microsection metallographic specimens prepared by a standard procedure. Grinding is carried out with sandpaper (P493, P600, P3000) with abundant water cooling. The final step of samples grinding includes using a diamond paste and a felt cloth. The metallographic analysis was performed using an Axiovert-40 MAT microscope. The microstructure and phase composition of the alloys, and topography of the pore wall surface were examined under scanning electron microscopes (Philips SEM 515 and Quanta 200 3D). Phase composition was studied using a Shimadzu XRD-6000 diffractometer with CuKα-irradiation. The porosity and apparent density were determined by weighing technique using analytical balance A&D GH-200. The pores size and pore intersections was determined by a combination of the secant method and the method of inscribed spheres

We have made a quantitative description of the pore structure. The porosity was found by the weighting method and calculated by the following formula:

$$P = (1 - m_{pore}/m_{cast})*100\%,$$

where m_{pore} is a mass of the porous sample and m_{cast} is a mass of the (may be solid) cast sample.

The specific surface area was determined by random ΣS intersecting, based on the second stereometric ratio [5]

$$\Sigma S = 2m,$$

where m is a average number of intersections per millimeter.

3 Results and discussion

Macrostructure studies of the TiNi porous samples obtained at the temperature of synthesis beginning of 400 °C have showed that a pore space occupies 75 % of the total material. It consists of a plurality of interconnected open pores and several amount of closed and deadlock pores. A distinguish feature of the resulting porous material is a homogeneous microporous structure with a narrow distribution of pore on sizes. A histogram of pore sizes distribution has a unimodal character, which is typical for small-pore materials. The average pore size is dpor=150 μm.

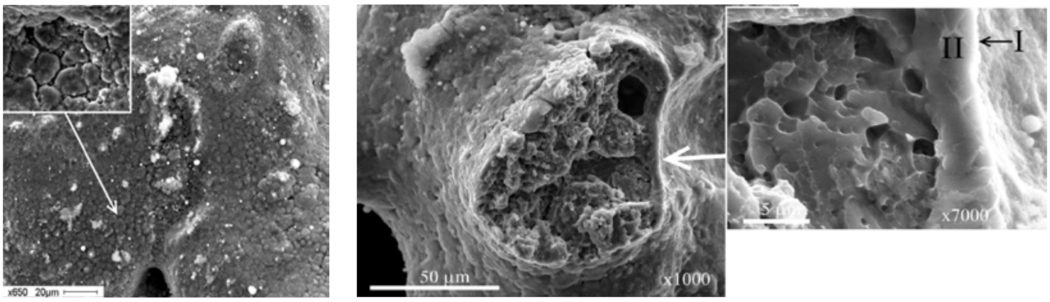
The formation of the porous space structure depends on an action of adsorbed gases that are filtered through the reacted portion of the sample [2, 6]. The intense gas evolution in the combustion wave improves pattern formation temperature zone. This increases the amount of the eutectic melt, which rapidly wets the powder mixture and then promotes coalescence. The morphological structure of the metal matrix TiNi produced by SHS, typical of highly porous materials produced with liquid phase participation. The specific surface area is Ssp = 31.7 mm^2 / mm^3. A complex surface is due to the presence of a system of open and interconnected pores, as well as a variety of recesses and protrusions on the walls of the pore walls.

A formation of the surface layer in a porous material is dictated by nonequilibrium diffusion processes occurring in a crystallization step. According to the phase diagram, the crystallization of TiNi system begins at the temperature of 1378 °C with formation Ni-rich phase TiNi3. Further, the crystallization temperature near an equiatomic compound TiNi is 1240 °C, and least Ti2Ni type phases form at T=1015 °C. Thus, firstly Ni-rich regions crystallize. In the process of phase separation during crystallization of such regions the TiNi grains with TiNi3 particles forming in the body and at the grain boundaries. At the temperature of 1015 °C during crystallization of peritectic melt the Ti2Ni phase forms at boundaries and in the body of formed TiNi grains formed.

The processes of phase separation occurring during crystallization of extremely heterogeneous composition of TiNi melt lead to appearance of dendritic zones with dendrites bodies similar to TiNi composition and interdendritic layers based on Ti2Ni phase. Dendritic segregation zones have a thickness from 10 to 15 μm and locate on pore edges. Dendrites body size is 5–10 μm with interdentritic layer thickness of 2–3 μm. Enriched peritectic melt under the influence of the solidification front is displaced on the surface of the pore wall, forming a characteristic dendritic relief (Fig. 1, a).

On the surface of pore walls the peritectic melt Ti_2Ni comes into diffusion interaction with gas impurities of carbon, nitrogen, oxygen, highlighting in the process of synthesis at an interaction of mixture components. Thus, a surface layer up to 12 μm thick is located usually in open pores, where the influence of the synthesis atmosphere gas has a maximum value. The layer thickness has a minimum value in dead-end and closed pores, where an action of gases on the surface is practically excluded.

It is found that the surface layer of a metallic matrix has a variable thickness and consists of oxycarbonitrides with inclusions plurality of different particles. The surface layer has its own substructure, consisting of carbonitride and oxynitride layers, which is confirmed by X-ray microanalysis (Fig. 1, b). An assumption of the layered structure of the surface oxycarbonitride layer is made on the basis of data on the separate crystallization of carbides, nitrides and oxides based on Ti_2Ni phases that have different formation enthalpy $Ti_4Ni_2C > Ti_4Ni_2N > Ti_4Ni_2O$ [7]. Moreover, their crystallization temperatures are also varied. Apparently, the crystallization process begins from a thin surface carbonitride layer with thickness of 50–100 nm (Fig. 1, b, marked I) [8]. Thereafter, oxynitride layer with 3–12 μm thick crystallizes (Fig. 1, b, marked II).



a b

Fig. 1. The surface structure of the pore wall of the porous TiNi obtained at synthesis beginning temperature of T=400 °C: a–the output of dendrites bodies on the surface, b–enlarged fragment of the surface layer: I–oxynitride layer; II–carbonitride layer

Many inclusions of secondary phases in the surface layer structure complicate an inner structure of the surface of pore walls. A high content of secondary phases is found, which have spherical shapes of different sizes. They are arranged individually or form large amorphous conglomerates on projections of the metal matrix. A large amount of particles is associated with high titanium activity at high temperatures and its segregation at a free surface. In a gas environment it is actively oxidized forming compounds with carbon, nitrogen, oxygen, the presence of which is marked on the surface of pore walls (Fig. 2). In addition, after the passage of the combustion wave under the action of a crystallization front, a lot of slag is displaced on free surfaces of the pore space. These clusters are located unevenly on the surface of the pore walls.

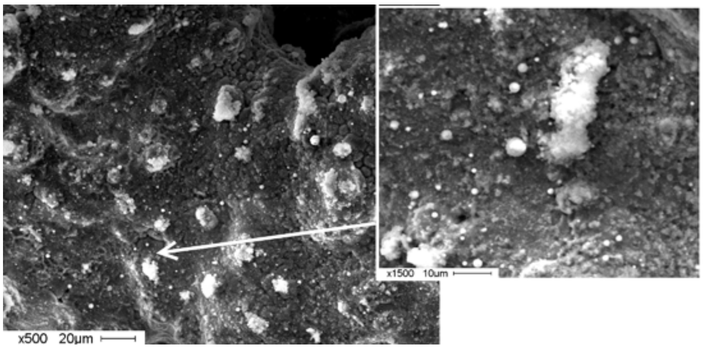


Fig. 2. The surface of the wall structure of the pores of the porous TiNi: surface layer with inclusions of secondary precipitates

Developed rough surface of the pore walls has a plurality of nano- and micropores in its structure except a complex oxycarbonitride layer and secondary selections. Dimensions of these pores are in the range from 0.01 to 1 μm. Such microtopography is formed during alloy solidification. Many phenomena related to segregation and growth of dendritic structures on pore edges leads to the appearance of the characteristic cellular surface topography (Fig. 1, a). The presence of micropores and their size distribution was confirmed by mercury porosimetry (Fig. 3).

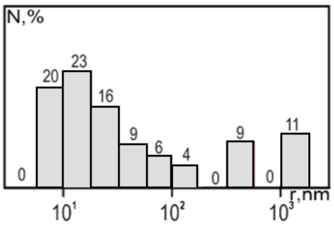


Fig. 3. The size distribution of nano- and micropores of the pore walls surface

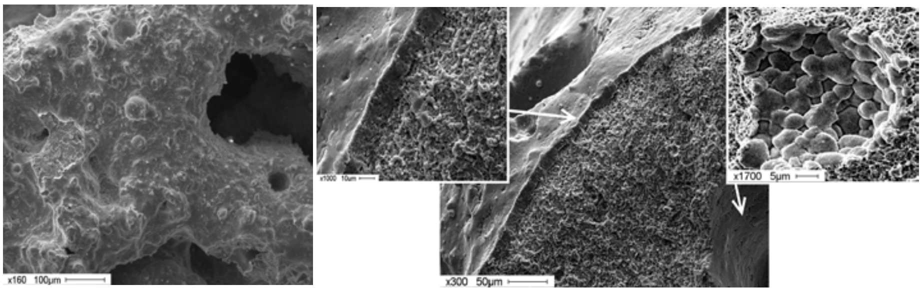
Production of porous TiNi at high temperatures of synthesis beginning (T>400–600 °C) is determined by the need to manufacture a material with a more homogeneous phase and chemical composition. At the same time a regular porous structure is kept due to a moderate temperature in the combustion wave. The synthesis beginning temperature T=600 °C is the maximum possible when a combustion takes place in the mode of continuous layered synthesis and processes of pores coalescence do not have clear character. Otherwise, the resulting material at higher temperatures becomes structurally unstable. The overabundance of a liquid phase results to an active coalescence and formation of cavities.

The material obtained at the temperature of synthesis beginning of T=600 °C refers to materials with a high porosity of 65 %. The average pore size is 310 µm. During passage of the combustion wave the powder system is wetted with melt of eutectic liquid. Due to capillary forces the large interporous jumpers with a smoothed relief of pore walls surface. The surface of metallic matrix has a uniform structure with a number of protrusions and depressions (Fig. 4, a). The specific surface area is 13 mm2/mm3.

Along the pore edges the presence of dendritic segregation zones was established, the thickness of which in some places is up to 40 µm. Although inceasing temperature of the synthesis beginning led to a more uniform phase chemical state of TiNi metal matrix, but not to a full escape of the processes of alloy segregation. Within a short time of existence of the liquid phase the processes of dendritic segregation lead to the emergence of cellular relief on the pore walls edges in some places. The size of dendrite body is from 10 to 30 µm , with ainterdendritic layer thickness of 2–5 µm.

The resulting material is characterized by presence of a dense bulk surface layer from oxycarbonitride with variable thickness (Fig. 4, b). Due to the segregation of active processes and oxidation of Ti-rich peritectic liquid the layer thickness in some places is 20 µm. In the open pores the dendritic structure of the surface of pore walls is practically undetectable because of the massive surface layer and a maximum interaction with synthesis gas medium. To identify cellular dendritic structure is possible only in closed pores, where the synthesis gas medium action is practically impossible.

X-ray microanalysis of the surface layer defined a large number of elements of implementation–carbon, nitrogen, oxygen in its composition except titanium and nickel atoms. Thus, with increasing temperature of synthesis begining the oxycarbonitride layer thickness increases due to a higher value of titanium segregation on available surfaces and its interaction with the high-temperature synthesis gas atmosphere.



a b

Fig. 4. The surface structure of the metal matrix (a) and the pore walls in open and closed pores (b)

It is found that at the initial temperature of synthesis to T=600 °C a material may be prepared with a minimum of secondary phases in the pore space (Fig. 5, a).After passage of the combustion wave in the area of heat dissipation and in area of a structure formation an increase in the temperature leads to a more complete chemical conversion process of TiNi compound. Due to this process a concentration heterogeneity is reduced both in the combustion wave and in the finished product, though it is still significant in consequence of a low time of melt being. On the surface of pores walls spherical and irregular shaped particles were observed which contain an increased content of carbon and oxygen.

Due to higher temperatures in areas of afterburner and heat emission than in the case of obtaining material at T=400 °C and a longer periods of existence melt TiNi respectively the alloy formation process occurs with a minimal amount of secondary phases. The alloy formation processes are completed, and a more homogeneous microstructure of the surface of pore walls is formed, which is substantially free of precipitates and cellular dendritic terrain hidden by the oxycarbonitride massive surface layer.

Mercury porosimetry data confirm the minimum number of micropores in the material (Fig. 5, b). Maximum micropore size distribution is in the range of more than 10 microns, the smaller pores are practically absent due to the less pronounced cellular structure and massive oxide layer with a minimum number of secondary inclusions.

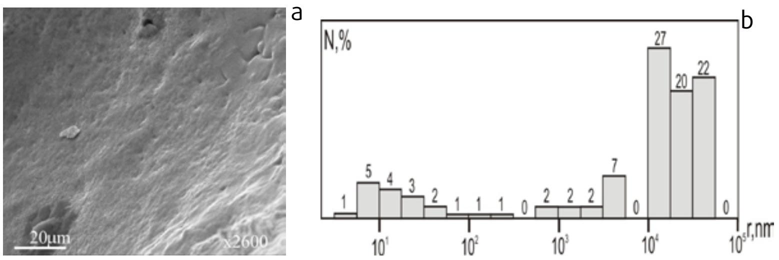


Fig. 5. The surface structure of the pore walls of the porous TiNi a–the oxide surface with a minimal amount of secondary phases; b–the data mercury porosimetry

Thus, the porous TiNi alloy obtained at the temperature of synthesis beginning of T=600 °C is characterized as a coarse material with heterogeneous macrostructure due to a wide range of pore sizes and interporous jumpers. Nano- and micropores are practically absent. The dense surface oxycarbonitride layer with a variable thickness is substantially free of secondary inclusions. Obtained SHS material by this manner has a phase-homogeneous chemical composition of TiNi metal matrix, which corresponds to TiNiequiatomic composition. The content of secondary phases is significantly decreased as compared with the material obtained at T=400C °C that indicates to the more complete alloy formation processes.

Analysis of TiNi porous structure has showed that the material obtained at the temperature of synthesis beginning of T=400 °C has a rough microporous surface of pore walls with a plurality of secondary phases of different origin. The oxycarbonitride surface layer of complex composition was found. Processes of phase separation during crystallization result in the formation of dendritic structures, which have a characteristic relief on the surface of pore walls. Phase and chemical composition of the material is very heterogeneous.

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