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Segregation in Porous NiTi Fabricated by SHS in Flow Reactor

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Abstract

The research considers the contribution of gases to the surface formation during self-propagating high-temperature synthesis (SHS) of porous titanium nickelide based alloys. The structure of the obtained porous alloys was analyzed using the methods of secondary ion mass spectrometry (SIMS), optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Nanocrystalline intermetallic oxycarbonitrides of a complicated structure were found on the porous titanium nickelide surface. A dense double gradient layer was found under the outer loose deposits. It is concluded that the dense gradient layer of intermetallic oxycarbonitride provides chemical passivity of the investigated porous alloys. Loose surface deposits of intermetallic oxycarbonitrides ensure successful integration of the alloy into the biological tissue in case of implantation.

1 Introduction

The surface properties are crucial for biocompatibility of porous titanium nickelide implants [1]. Corrosion resistance and biocompatibility of implants with living cells depend on the microrelief, structure and phase composition, and physicochemical properties of the surface, which are strongly dependent on methods used for porous alloy production. Methods for creating coatings on implant materials made of corrosion resistant titanium carbides and nitrides and intermetallides are widely used to make corrosion resistant and biocompatible implants. The surface can also be modified through treatment with laser, ion and electron beams, which allow creation of nanocrystalline and amorphous gradient layers of corrosion resistant compounds [2].

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Selective solidification of intermetallic carbides, nitrides and oxides based on the Ti_2Ni phase has been shown in the [3], since the enthalpy of formation decreases in the order $Ti_4Ni_2C > Ti_4Ni_2N > Ti_4Ni_2O$.

2 Experimental

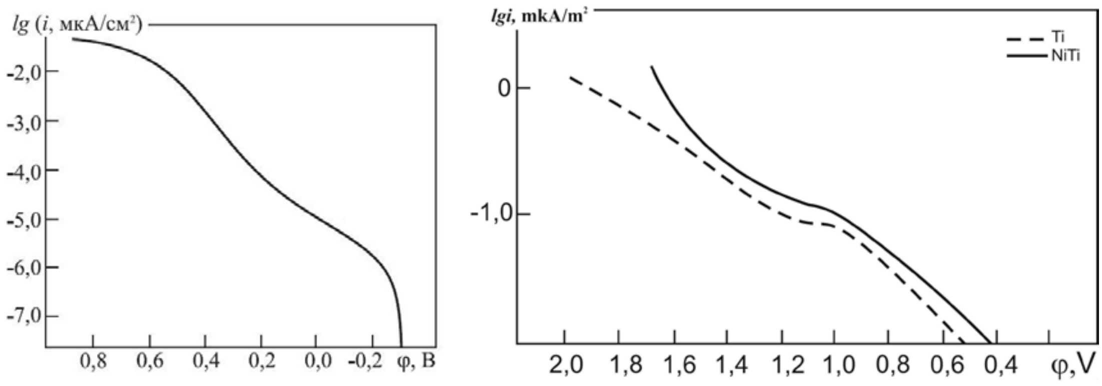
Anodic behavior of porous titanium nickelide produced by SHS method and that of modified monolithic titanium and titanium nickelide were studied in electrochemical cells by potentiodynamic polarization. The porous titanium nickelide based alloy was polarized in phosphate buffered physiological solution at human body temperature in compliance with ASTM standards G61 [4]. Monolithic flat samples of titanium and titanium nickelide modified by anodic polishing followed by nitrogen ion implantation were polarized in a 1% aqueous solution of hydrochloric acid. Anodic polishing was carried out in acetic-chloride electrolyte through stirring and cooling electrolyte to make the anode layer homogeneous and transparent. Nitrogen ion implantation was performed using an ion source with the following parameters: 60–80 kV accelerating voltage; 0.A current; 400 μs pulse duration; 50Hz frequency; 250 cm^2 beam cross-sectional area; 10^{16} irradiation dose.

Porous titanium nickelide based alloys are produced from titanium and nickel powders by powder metallurgy methods including SHS. In the experiment, SHS was conducted in protective gas medium, which is crucial for the procedure. Inert gas used as protective atmosphere displaced the air after filtering through the charge and reaction products at excessive pressure of 0.01–0.05 MPa and thus prevented oxidation of the charge and the product. The test samples were prepared from titanium powders RP-Ti grade OM (Russia Tula) [5] and carbonyl nickel powder L5 (Russia Norilsk) [6] by SHS method in a flow reactor. The corrosion resistance of porous samples was evaluated in compliance with ASTM standard G61.

The samples were prepared in accordance with standard procedures for titanium alloys. Electrochemical etching of samples for SEM was performed in acetic-chloride electrolyte. The study was conducted using SIMS (CAMECA IMS 4f), SEM (Philips SEM 515, QUANTA 200 3D), and TEM (JEM-2100F) with specimen preparation system EM-09100IS Ion Slicer (JEOL). The samples for TEM were prepared using QUANTA 200 3D with intentional deposition of the protective platinum layer. Optical microscopy was performed using the inverted optical microscope Axiovert 40 MAT.

3 Results and discussion

The comparative analysis of the anodic dependencies of potentiodynamic polarization showed (Fig. 1) that monolithic titanium nickelide samples modified by anodic oxidation and nitrogen ion implantation with carbon impurities behave in chloride-containing media similarly to porous titanium nickelide not subjected to any additional treatments [7].

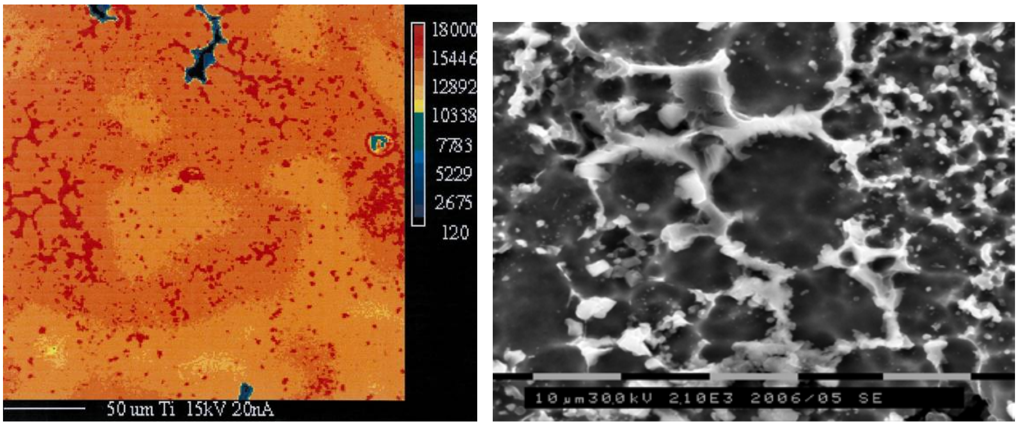


a b

Fig. 1. Anodic behavior of (*a*) porous titanium nickelide made by SHS without further treatment and (*b*) monolithic titanium and titanium nickelide samples modified by anodic polishing followed by nitrogen ion implantation

This suggests the presence of surface layers of intermetallic oxycarbonitrides on the surface of the porous titanium nickelide obtained by SHS, which provide it with corrosion resistance properties comparable with that of metalloceramic composites.

During SHS of porous titanium nickelide, glowing of different intensity was repeatedly observed in the local regions of the reaction zone. These observations suggest thermal heterogeneity of the reaction zone and this corresponds to the experimental results obtained in the study of different SHS systems reported by other authors [8–10]. They showed that the heat released during the reaction in SHS is distributed as self-similar traveling waves, and the reaction front has a fractal structure. In our experiment, we found that thermal heterogeneity of the reaction zone is accompanied by chemical heterogeneity of the synthesized titanium nickelide (Fig. 2a) and microsegregation of titanium in the solidification zone of the alloy (Fig. 2b).



a *b*

Fig. 2. Chemical and phase heterogeneity of porous titanium nickelide produced by SHS: distribution of Ti concentration. SIMS CAMECA IMS 4f. Microsection (a). Region of peritectic solidification and solid solution in the porous $Ti_{50}Ni_{50}$ alloy made by SHS. SEM. Microsection. Electrochemical anodic etching (b)

The regions with average titanium content correspond to the TiNi solid solution. The greatest titanium content is observed in peritectic solidification regions, particularly in the grain-boundary phase. The titanium content in secondary segregations of the solid solution is approximately the same as that in the grain-boundary phase in the peritectic regions. The titanium distribution in the regions of higher titanium content in the Ti-Ni system corresponds to TiNi and Ti_2Ni compounds and indicates dendritic microsegregation.

Dark TiNi grains 5–20 µm in the peritectic solidification region are surrounded by dendrites of light Ti_2Ni phase (Fig. 2b). The Ti_2Ni phase crystals and slag inclusions, which are not found in the grain body, are adjacent to the dendrites.

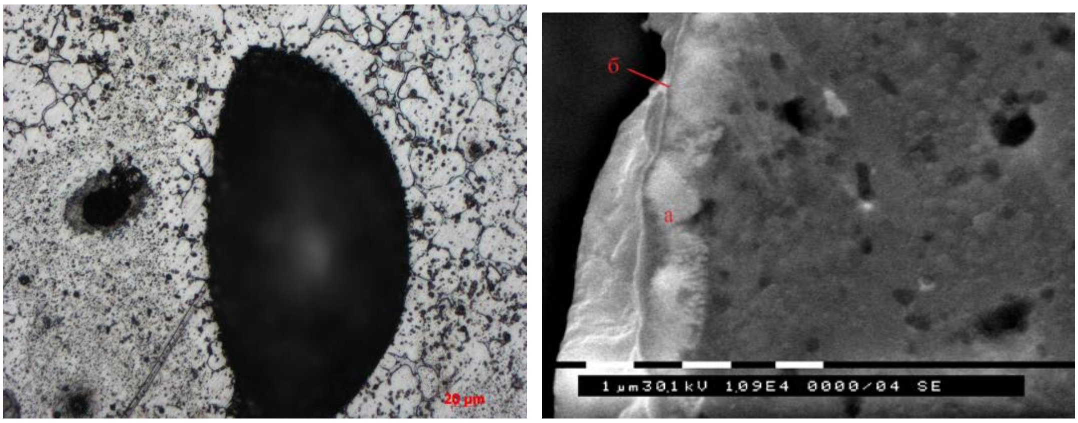
The right part of the image shows the region of solidification of the solid solution containing coarse secondary segregations and numerous slag inclusions. However, segregation dispersion in this region is higher than that in the peritectic region. Despite a weak grain-boundary phase in the solid solution region, the size of grains not exceeding 5 µm can be evaluated.

The experiment revealed that the delay (within a fraction of a second) of the porous alloy in a solid-liquid state at the stage of solidification leads to the pore coarsening and increases dendritic microsegregation. This is due to the heat transfer from the reaction zone to the structure formation zone by flow gases.

Both pores and regions of dendritic microsegregation are always located in peritectic solidification regions (Fig. 3a). The pores are mergered due to the grain-boundary melt of the low-melt Ti_2Ni phase to ensure the mobility of rounded TiNi grains. The Ti_2Ni phase melt occurs after titanium microsegregation and provides peritectic solidification.

The highly porous granular macrostructure with rounded grains is typical of both SHS systems with a melting phase [11, 12] and peritectic alloys [13].

Gaseous titanium and nickel impurities evolving in the reaction zone are the main source of gases during SHS of titanium nickelide. The temperature of the impurities is close to 1300° C, and they play an important role in the formation of a complex structure of the porous alloy surface.



a *b*

Fig. 3. Granular peritectic regions of $Ti_{50}Ni_{50}$ alloy obtained by SHS prior to homogenization annealing: optical microscopy of the region around macropores (a); SEM image of the fragment of the region, including double surface layer (b)

Both melt and gases are heat and mass transfer agents, which provide mutual influence during SHS of porous titanium nickelide. When leaving the reaction zone, flow reaction gases exhibit high temperature, pressure and velocity. Due to this, they capture a portion of the melt on the surface of small dead-end pores and distribute it to larger open pores to form loose deposits on their surface (Fig. 4a).

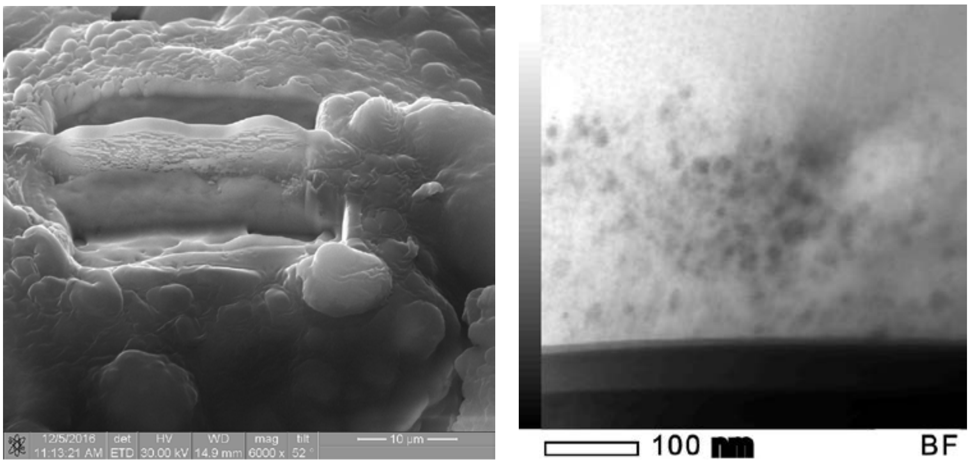


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Fig. 4. The structure of the surface layers of porous titanium nickelide obtained by SHS: a general view of the sample with loose deposits on the surface. The deposited platinum layer can be seen on the surface. QUANTA 200 3D (a); TiNi matrix, double layer and loose layers of intermetallic oxycarbonitrides. TEM JEM-2100F (JEOL) (b)

The melt composition is close to the stoichiometry of the Ti_2Ni intermetallide. Simultaneously, the melt is saturated with oxygen, nitrogen, carbon and hydrogen impurities typically observed in the reaction gases. Therefore, solidified deposits appear as intermetallic oxycarbonitrides. A residual layer of the peritectic melt is found under the newly brought layers. It is also saturated with impurities of the reaction gases and solidifies into an oxicarbonitride layer (Fig. 4b). Due to the different enthalpy of formation and solidification temperature of carbides, nitrides and oxides $Ti_4Ni_2C > Ti_4Ni_2N > Ti_4Ni_2O$, the intermetallic surface layer is solidified with the gradient of concentration, density and size of nanograins and becomes double with a thickness of about 50–100 nm.

This thin layer of the solid solutions of oxygen, nitrogen and carbon based on the Ti_2Ni phase provides the chemical passivity of the surface of the porous titanium nickelide shape memory alloy, that it was discovered experimentally in the electrochemical and clinical studies [1].

The unique complex of high physicomechanical and physicochemical properties enables application of the porous titanium nickelide alloy made by SHS in various fields of medicine.

4 Summary

Microsegregation affected by thermal influence of the reaction gases flowing through the pores of the synthesized alloy develops under the pore surface. As a result, biphasic peritectic regions appear, where one of the phases, rounded grains of the TiNi intermetallide, is surrounded by the second phase, shells of the Ti_2Ni intermetallide.

The surface of the Ti_2Ni phase melt interacts with reaction gases and solidifies to form a dense double layer of nanocrystalline intermetallic Fig. 1. Anodic behavior of (*a*) porous titanium nickelide made by SHS without further treatment and (*b*) monolithic titanium and titanium nickelide samples modified by anodic polishing followed by nitrogen ion implantation.

Reaction gases capture a portion of the Ti_2Ni phase melt in fine pores and transfer it to large pores, thus creating loose deposits of nanocrystalline intermetallic intermetallides on the pore surface.

Surface nanocrystalline intermetallic oxycarbonitrides make the porous titanium nickelide electrochemically passive.

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