Shell structure of the porous TiNi-framework obtained by the SHS method

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Abstract. Porous SHS-TiNi alloys, presented as a porous framework with a complex structure of the Core-Shell type, were studied by microscopic and structural methods. The core is the porous framework of an intermetallic TiNi phase. The shell was found to be a complex three-layer complex. An oxygen-hardened peritectic TiNi–T1Ni layer 1-6 μm thick forms an inner shell layer. Thermo and corrosion-resistant amorphous-nanocrystalline intermetallic oxycarbonitrides, saturated with O, N, C interstitial impurities, form middle and outer layers. The middle dense double layer 60-80 nm thick protects the TiNi matrix. The outer layer 1-15 μm thick has a loose layered structure, it is enriched in the MAX-phases T1SiC2, T1AlC2. The dense nano double layer provides a chemical passivity to the porous nickelide titanium alloy with shape memory, does not limit mobility and improves the ability to integrate into biological tissues.

1. Introduction
Porous TiNi-based intermetallic alloys obtained by self-propagating high temperature synthesis (SHS) are used in clinical practice. They possess biocompatibility, which is confirmed experimentally [1,2]. The phase composition and structure of the surface layers completely determine the morphological features of the surface and the biochemical compatibility of implants with biological tissues.

The morphology, phase composition and structure of porous alloys of the Ti-Ni system have been studied in many scientific works, which show that these alloys almost always contain inclusions of intermetallic oxycarbonitrides T1Ni2(O,N,C), as well as titanium oxides, carbides, and nitrides of various stoichiometry [3-6]. Their presence is due to the high cost of purifying reagents and reaction products from interstitial impurities [7].

The SHS method has features that allow the creating of porous alloys with increased corrosion resistance, compared with the reaction sintering method of Ti-Ni system alloys [8,9]. They successfully resist the corrosive effects of a chlorine-containing medium due to the surface shell. However, the phase composition and structure of the surface layers of porous SHS-TiNi alloys have not been studied sufficiently, therefore, studies on this solve remain relevant.

2. Material and methods
Self-propagating synthesis reaction of the TiNi alloy was carried out through layer-by-layer regime. We used titanium powder reduced with RP-Ti grade OM-2 by POLEMA (Russia) and Carbonyl Nickel Powder PNK-1L5 by NORILSK NICKEL (Russia). The porous alloy was disintegrated into granules by impact destruction. The granule filling was annealed in a vacuum at a temperature of 1200 °C for 40 min. An annealing was carried out in order to diffuse the granules sintering.
The structural-phase composition of the surface was studied by XRD analysis using an XRD-6000 diffractometer with Cu Kα radiation. The POWDER CELL 2.4 full-profile analysis program was used to process the diffraction pattern. Optical micrographs were obtained by means of Carl Zeiss Axiovert 40 MAT light microscope and the Focus stacking technique. Confocal laser scanning microscopy was performed on a surface area of 30×30 mm of a porous sample using irradiation lasers with characteristic excitation wavelengths of 405 and 488 nm and ChS1 filters: 517-695 and 410-695. Electron microscopic studies were carried out using a JEM-2100F microscope (JEOL). The lamella for TEM was prepared on QUANTA 200 3D. Plates were cut 0.7 mm thick, 7 mm wide and 80 mm long from porous SHS-TiNi samples. The plates were destroyed on an Instron installation by tensile strain. Fractogram analysis of fracture surfaces was carried out using a QUANTA 200 3D scanning electron microscope in SEM mode.

3. Results and discussion

Confocal laser scanning microscopy (CLSM) of polished porous SHS-TiNi samples shows a presence of the shell (green color) on the porous framework, marked C (Fig.1, inset 1). The shell of the porous framework is also clearly visible due to its brightness on the optical microscopy image in the dark field, in contrast to the dark cross-section surface (Figure 1, inset 2).

![Figure 1](image)

Figure 1. Scheme of shell view by various types of microscopy: 1 - CLSM; 2 - light microscope cross section in a dark field; 3 - SEM after impact failure; 4, 5 - light microscope cross section in a bright field; 2, 4 - before annealing; 5 - after annealing.

The shell is a feature of the SHS process of intermetallic compounds, and it is formed during the interaction of reaction gases with the melt film on the surface of the porous framework [10]. Due to the heat of the reaction gases along the walls of large pores, in the zones of peritectic crystallization, the internal structure of the framework is enlarged: the intergranular peritectic Ti2Ni phase and TiNi grains (Figure 1, inset 4). The Ti2Ni phase is more saturated with oxygen and hardens than other phases in the Ti-Ni system. The TiNi phase less dissolves oxygen, but partially loses titanium. A change in composition towards nickel enrichment induces it to go into a martensitic state. This leads to the
hardening of TiNi grains. Thus, a hardened layer is formed, which is destroyed by a brittle mechanism under shock loads (Figure 1, inset 3). In contrast, a non-hardened matrix of the framework is destroyed by a viscous mechanism.

The thick of the hardened shell is determined by the depth of oxygen diffusion and reaches 1-6 μm. The surface layer prevents sintering the granules of the porous framework in a vacuum (Figure 1, inset 5). At an annealing temperature above 1200 °C, the TiNi phase becomes viscous and easily deforms under the influence of surface tension forces. However, the dense contact of granules does not lead to the formation of diffusion necks between them, even when holding for 40 minutes. The presence of volume diffusion and the absence of surface diffusion indicate that the surface layer is refractory. Previously, the annealing of TiNi powder under the same conditions led to the formation of diffusion necks between the particles and a complete change in their morphology as a result of surface and bulk diffusion.

It was previously established that the surface of the porous SHS-TiNi is corrosion resistant [11]. The surface part of the shell was detected at TEM in the form of a double layer 60-80 nm thick (Figure 2). Chemisorption of dissociated reaction gases by a titanium-enriched melt occurs during peritectic crystallization at the beginning of the structuring zone. Therefore, we found the double layer even in alloys with small pores in the range of 50-70 μm, which did not have time to grow larger.

![Figure 2. Scheme of shell structure](image)

Figure 2. Scheme of shell structure

Chemoepitaxy forms the double carbonitride film on the liquid surface of the melt in two stages. At the first stage, as a result of chemisorption of O, N, C, Si, Al impurities from the reaction gases, an amorphous Ti-Ni-C-N-O-Si-Al film is formed on the peritectic liquid surface. At the second stage, as a result of the crystallization of the amorphous Ti-Ni-C-N-O-Si-Al film, the epitaxial growth of nanocrystalline phases Ti$_2$Ni$_2$O(N,C), Ti$_2$Ni$_2$O, Ti$_3$SiC$_2$, Ti$_3$AlC$_2$ occurs.

Considering the capability of the Ti$_3$Ni intermetallic compound to amorphize under the influence of interstitial impurities, the amorphous phase of intermetallic oxycarbonitrides is formed after the passing the synthesis wave. At the structuring stage, the amorphous phase crystallizes under the thermal influence of the reaction gases and turns into amorphous nanocrystalline. It is known that such amorphous – nanocrystalline phases have high strength and corrosion resistance [12-14].

A liquid layer of the peritectic shell of TiNi grains, whose composition is close to the stoichiometry of the Ti$_3$Ni, remains under surface amorphous film after its hardening. This allows the framework, which consists of viscous TiNi grains, liquid interlayers, a solid, but thin shell, to remain in a mobile state throughout the entire structuring stage of the porous alloy. In this case, under the influence of the reaction gases heat, the pores merge and enlarge, as well as framework walls thicken.
The reaction gases, flowing out of the reaction zone, capture part of the melt and carry compounds of impurities with titanium: Ti$_4$Ni$_2$O, Ti$_3$SiC$_2$, Ti$_3$AlC$_2$ in the form of an aerosol over the structuring zone. Thus, loose layers are formed on the surface of the double dense layer.

Qualitative XRD analysis has shown that the main component of the surface layer is the amorphous-nanocrystalline phase of intermetallic oxycarbonitrides Ti$_4$Ni$_2$(O,N,C), which is a solid solution of O, N, C in the peritectic Ti$_2$Ni phase. Diffraction reflections from cermet ternary MAX phase Ti$_3$SiC$_2$ with a nanolaminate structure and the intermetallic matrix TiNi B2 were revealed in the diffractograms.

Figure 3 shows a TEM image of surface layers with corresponding SAED patterns. The Ti$_4$Ni$_2$O phase with residual amorph was detected in all layers. Diffraction patterns 1 and 2, taken from loose and dense nano double layers, show a diffuse halo near small diffuse reflections of the Ti$_4$Ni$_2$O phase, which indicates an amorphous-nanocrystalline state. The previously obtained XRD spectrum from the surface of the SHS-TiNi shell contains an amorphous halo and diffuse X-ray reflections of Ti$_4$Ni$_2$O with CSR=7 nm, which confirms its amorphous-nanocrystalline structure [15]. Particles of the Ti$_4$Ni$_2$O phase of globular shapes were found in the hardened layer, their corresponding diffraction pattern 3 is characteristic of a fully crystalline structure.

![TEM image of the shell with corresponding SAED patterns](image-url)

**Figure 3.** The TEM image of the shell with corresponding SAED patterns

**4. Conclusions**

1. It was experimentally shown that, as a result of the interaction of reaction gases with the peritectic melt in the SHS process, on the porous TiNi-framework the shell is formed. The shell consists of the inner hardened layer 1-6 µm thick and the outer corrosion-resistant nanocrystalline layer 15 nm-15 µm thick.
2. The corrosion-resistant nanocrystalline layer was shown to also consist of the inner dense double layer with a thickness of 15-60 nm and the outer loose layer 0-15 µm thick. The dense inner layer is formed by intermetallic oxycarbonitrides Ti$_4$Ni$_2$(O,N,C). The outer layer is formed by oxycarbonitrides Ti$_4$Ni$_2$O and MAX-phases Ti$_3$SiC$_2$, Ti$_3$AlC$_2$.
3. Due to the thermal and corrosion resistance, the dense double nanocrystalline layer provides reliable protection of the porous TiNi-framework both during electrochemical and gas corrosion. The small thick of the inner double layer and the friability of the thicker outer layer do not limit the mobility of the superelastic framework. The loose multi-layer structure of MAX-phases provides good integration into biological tissues.
5. References

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