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Production of Two-Dimensional Porous TiNi-Based Powder Material by Diffusion Sintering and Electron-Beam Processing

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***Abstract*—The paper addresses the study of the surface condition of two-dimensional porous TiNi-based powder materials produced by diffusion sintering and electron-beam processing. Methods of production of two-dimensional TiNi-based materials to be used for the purposes of non-destructive testing have been proven. The surface condition of the produced materials is described by scanning electron microscopy and interference profilometry.**

Keywords—TiNi alloy, powder metallurgy, diffusion sintering, electron-beam process, structure, terraced relief, roughness.

I. Introduction

Physico-mechanical and structural characteristics of porous and monolithic TiNi-based materials fabricated from calcium hydride TiNi powder have been studied in numerous papers [1–5]. The production conditions, structural-phase composition, and functional properties of sintered TiNi alloys are described in [6, 7]. However, one of the problems faced is impossibility of using non-destructive methods, including optical profilometry, for studying the condition of the porous material surface. The surface of porous material at the first stages of its interaction with the body affects the kinetics of implant integration; therefore, the data on its fine structure is of particular importance [8–10]. Thus, the chosen study area is relevant, especially for further practical use of porous TiNi-based materials in implantology.

Access to the developed internal structure of the porous material requires preliminary transverse fracturing. Stress fields and cracks can distort the surface structure of the pore walls, and the volumetric structure of the porous material can impede the study. To solve this problem, we attempted to fabricate two-dimensional (2D) porous samples with a structure similar to that of the porous body of TiNi alloy. Calcium hydride TiNi powder was placed on TiNi monolithic plates and sintered under similar conditions to produce porous TiNi materials. As a result, the structure of the porous body produced by diffusion sintering was identical. This approach will be effective in studying the surface morphology of the material using scanning, transmission and atomic force microscopy, and profilometry without pre-treatment of the test sample that could potentially distort the study results. In addition, modification of 2D porous materials by electron-beam processing will provide a new set of properties not attainable by other methods. Based on the foregoing, the aim of the study was to develop a method for producing 2D porous TiNi-based powder materials by diffusion sintering and electron-beam processing, and to investigate the surface condition of the materials produced.

II. Experimental Setup

The object of the study was porous TiNi-based materials produced by diffusion sintering (DS) and electron-beam processing (EBP). We used TiNi powder of PV–N55T45 grade to fabricate the porous body and a monolithic TiNi plate [11]. The powder was placed on a plate and uniformly distributed on its surface to prevent discontinuity of the layer. The thickness of the powder layer was about 300–350 μm, which corresponds to the size of 1–2 TiNi powder particles. TiNi powder was pre-dried in a dry oven at 150°C for 2 hours. According to the quality certificate, the average particle size was 140 μm with a fraction of 0–200 μm. The monolithic plates were produced by rolling of TiNi alloy using a two-roll mill. The billets made were 20 mm × 20 mm in size with a plate thickness of 1.5–2 mm. The plate surface was treated with sanding paper with a grain size index of P600.

The samples were fabricated by single diffusion sintering at a temperature of 1240–1260°C, and the sintering time was 15 min. The surface condition of the samples produced should

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correspond to porous sintered samples; therefore, the temperature-time regime chosen corresponded to that successfully tested in [4]. In order to minimize the amount of secondary phase particles on the material surface, sintering was performed in molybdenum parallelepiped moulds with dimensions of 25 mm × 25 mm × 5mm, which consisted of upper and lower sections. A plate with powder was placed in the lower section, and the upper section of the molybdenum mould was installed on top. Sintering of the molybdenum mould with the sample inside was performed in a quartz capsule at a chamber pressure of $6.65\cdot10^{-4}$ Pa with an average heating rate of 10°C/min. The proposed sintering scheme made it possible to eliminate the carbon-rich surface layers with a minimum content of particles of the secondary Ti_2Ni phase.

Two-dimensional porous materials were produced by electron-beam processing using the RITM-SP setup (Institute of High-Current Electronics SB RAS, Tomsk) equipped with a source of low-energy high-current electron beams of microsecond pulse duration [12]. The combined RITM–SP setup is designed to form thin layers of alloys on the sample surface in a single vacuum cycle (in situ). The setup includes a source of low-energy (10–30 keV) high-current (up to 25 kA) pulsed (2–4 µs) electron beams and a magnetron atomizer mounted together with the electron gun of the source on a vacuum operating chamber. To fabricate 2D samples from TiNi alloy powder by electron-beam processing, TiNi powder was placed on the monolithic plates (20 mm × 20 mm) in a layer of about 300–350 µm. During pre-manipulations in the RITM-SP setup chamber and electron-beam processing, the powder can disperse in the chamber volume; therefore, the powder sample was heated in the SNVE–1.31/–I4 electric vacuum furnace to 1200°C with an aging time of 15 min to fix individual powder particles. Inter-particle contacts are formed between the powder particles, and sintering proceeds through its initial stage, when the structure of individual particles remains unchanged. After this procedure, the billet for fabrication of 2D samples was placed in the chamber of the RITM-SP setup. The samples were exposed to electron beam with pulse duration of 2–4 µs and beam diameter of up to 80 mm. The samples were irradiated by electrons with high energy of 30 keV, while the energy density was $E_s \approx 6$ J/cm^2, and the number of the processing pulses was 30.

The macro- and microstructure of the fabricated samples was studied by scanning electron microscopy (SEM) using the Quanta 200 3D system with electron and focused ion beams at accelerating voltages of 20–30 kV. The concentration composition of the phases was determined using the EDAX ECON IV energy dispersive spectrometer. The MNP-1interference microscope and MNP-1 software were used to build three-dimensional surface reconstruction and determine roughness parameters.

III. Results and Discussion

Numerous individual TiNi powder particles adhered to the monolithic plate surface form the macrostructure of the fabricated samples (Fig. 1). The effects of DS and EBP are identical, and the macrostructure of the fabricated experimental samples is identical. The diffusion sintering temperature is chosen to enable the formation of the moderate portions of $TiNi+Ti_2Ni$ melt during high-temperature aging that partially dissolve the surface of the powder particles, forming interparticle contacts and new surfaces. Electron-beam processing at the chosen processing mode affects only the surface layers of the 2D sample based on TiNi alloy powder.

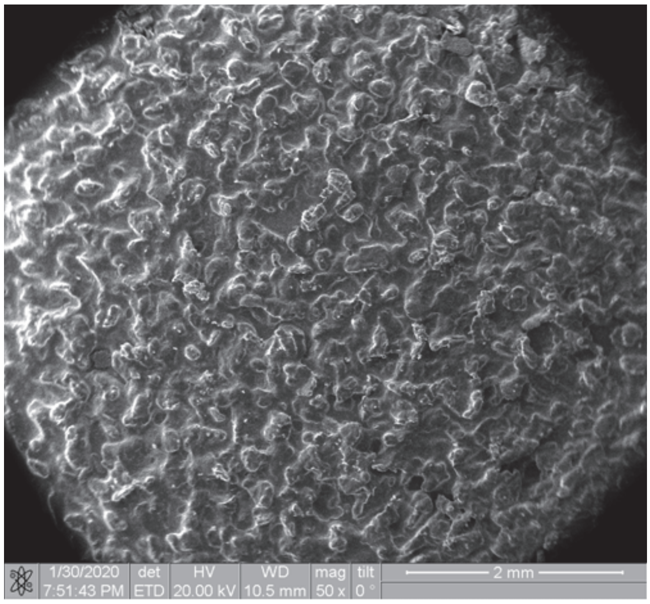

Fig. 1. Macrostructure of the surface of the 2D porous material produced by diffusion sintering and electron-beam processing.

Study of the microstructure of the surface of DS TiNi-based material showed that all TiNi junctions free of secondary phase particles exhibit a developed terraced relief characteristic of TiNi-based alloys obtained by DS (Fig. 2). Terraces are located in areas free of secondary phase particles and spread along the curved surface of the 2D porous powder material within the same grain, preserving the periodic structure. When moving from one grain to another, the terrace direction may change or remain stable depending on the grain orientation. The height of the ledges is up to 0.25 µm and the width is 0.4 µm –0.5 µm. According to the terrace–ledge–kink (TLK) model, adatoms are attached to the kink surfaces located on the surface of crystalline bodies to form the relief. The relief is formed due to the processes of surface diffusion of adatoms, volume diffusion of atoms and their interaction with substrate defects during melt crystallization.

Several sources contribute to the formation of spatial ledges of terraces: heterogeneity of the concentration of TiNi powder used for sintering and the effect of creep deformation. In the first case, heterogeneity of the concentration of the main phase of TiNi powder causes mutual diffusion and accelerates mass transfer during the formation of the porous structure. The effect of creep deformation caused by increased atomic diffusion under the impact of surface tension forces enhances the transport of substances and contributes to the formation of a liquid phase in sintering. At temperature close to the melting point, the TiNi phase undergoes a plastic flow, and the surface tension energy attains 1.775 N/m. This is confirmed by the studies reported in [13], which describe similar mechanisms leading to formation of this type of structure with hexagonal islands and terraces obtained by thermal etching of pure Ni.

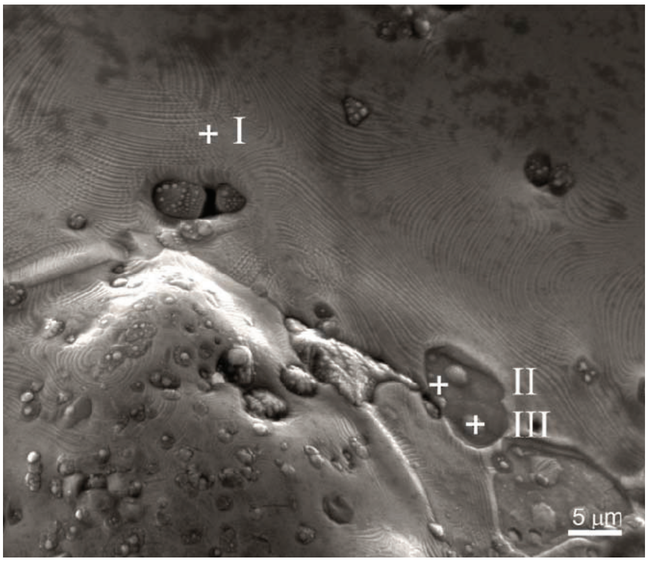

Fig. 2. Microstructure of the surface of the 2D porous material produced by diffusion sintering.

Diffusion processes responsible for mass transfer on the concave and convex surfaces of individual powder particles occur under heating and high-temperature aging during sintering. The nature of formation of the terraced relief under the impact of surface and volume diffusion of atoms is confirmed by the study of the microstructure of the EBP TiNi-based material surface. However, the time factor is crucial for the terraced relief formation, that is, the formation of the terrace ledges is a time-consuming process, and high energy of surface tension only is not sufficient for formation of terraces on the surface of TiNi alloy powder. This conclusion is based on the data on microstructure of the EBP material surface obtained in the study (Fig. 3). No terraced relief was observed on the EBP material surface despite the presence of new surfaces formed under the impact of the melt caused by high-energy electron beam. The surface morphology of the material is smoothed and contains an inconsiderable number of inclusions. The secondary phase particles based on Ti_2Ni and Ti_4Ni_2(O,N,C) oxycarbonitrides in the material structure are less in number, which can be attributed to homogenizing effect of electron-beam processing.

Additional justification of the time factor that affects formation of the terraced relief can also be found in the study of porous TiNi-based materials prepared by self-propagating high-temperature synthesis (SHS) [1, 6]. The structure formation in these materials occurs within milliseconds with sharp heating, melting, wetting, crystallization and subsequent cooling. High rate of the chemical reaction leads to inter-pore bridge segregation and formation of secondary phase particles based on Ti_4Ni_2(O,N,C) oxycarbonitrides, massive oxide layers of oxycarbonitrides up to 20 µm thick. The terraced surface relief of the pore walls is not found in SHS materials.

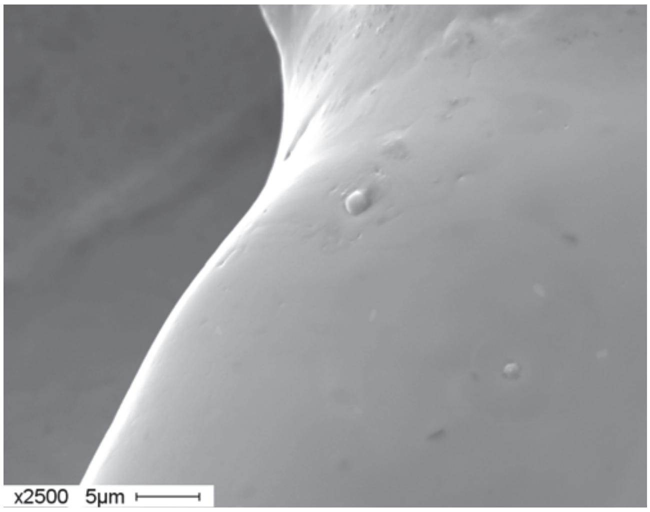

Fig. 3. Microstructure of the surface of the 2D porous material produced by electron-beam processing.

Study of the three-dimensional reconstruction of the surface revealed a difference between the roughness coefficients for DS and EBP materials, the nature of profilograms being similar for different materials (Fig. 4). The height of the sintered layer corresponds to single or paired particles of TiNi powder. The powder particles have a spongy and compact morphology with an irregular shape in the form of a deformed ellipsoid with flat vertices of 100–200 µm and a particle thickness of about 40–100 µm. The particle shape is the result of deformation during grinding after calcium hydride reduction. During adjustment of the grain size distribution and filling density, the roughness parameters can be changed in a wide range of values. For 2D materials produced by DS, the maximum profile height R_z = 300–400 µm, which corresponds to the geometric dimensions of the particles with surface roughness coefficient R_a = 85–115 µm. Increased sintering temperature causes formation of a larger amount of the liquid phase during high-temperature aging, a decrease in the specific surface and in the area occupied by the terraced relief, which reduces the coefficient R_a = 60–80 µm. Varying the temperature-time regimes of diffusion sintering can result in the material with different roughness coefficient R_a when using TiNi alloy powder.

Analysis of the roughness parameters of the 2D EBP material prepared from powder materials similar to those used for the 2D DS material showed a decreased roughness coefficient R_a and an insignificant change in the maximum profile height R_z.

A decrease in the roughness coefficient to R_a = 50–70 µm was observed due to a more smoothed morphology of the material surface. During preparation of the 2D material with a large TiNi powder fraction, electron-beam processing has only a surface effect at a depth of 5–10 µm. The revealed feature determines the grain size distribution of TiNi-based calcium hydride powder.

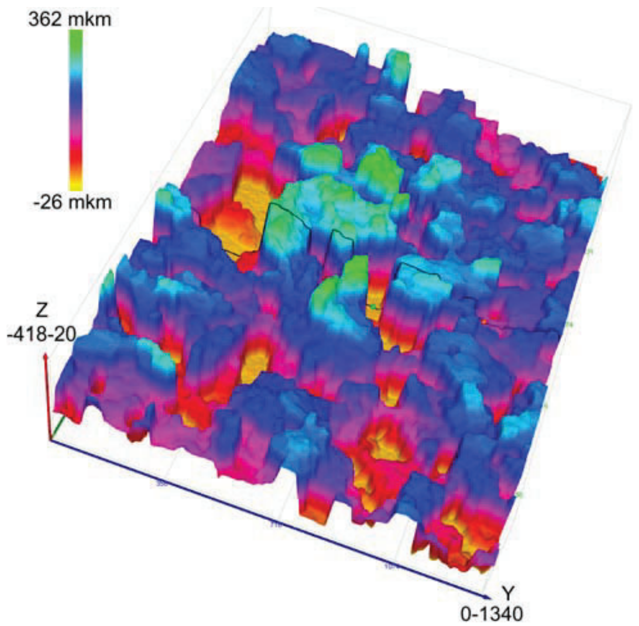

Fig. 4. Three-dimensional reconstruction of the surface relief of the 2D porous material produced by diffusion sintering and electron-beam processing.

IV. Conclusion

Thus, the study of the surface of 2D porous materials made from TiNi-based alloy powder obtained by diffusion sintering and electron-beam processing allows drawing the following conclusions. The effects of diffusion sintering and electron-beam processing are identical and can facilitate the creation of 2D porous TiNi-based materials. The macrostructure of the experimental samples obtained by various methods is identical. The diffusion sintering temperature is chosen to enhance formation of moderate portions of the TiNi+Ti_2Ni melt during high-temperature aging, which partially dissolve the surface of the powder particles and form inter-particle contacts and new surfaces. Electron-beam processing in production of 2D materials with a large fraction of TiNi powder has only a surface effect at a depth of 5–10 µm. The revealed feature determines the choice of the particle size distribution of calcium hydride powder based on TiNi in favor of a smaller powder particle size. A terraced relief is formed on the surface of 2D materials obtained by diffusion sintering only, which indicates a high value of the time factor during formation of terraced structures. The roughness coefficient of the 2D DS material is $R_a = 85–115$ µm, and the increased sintering temperature decreases the roughness coefficient to $R_a = 60–80$ µm. A more smoothed surface morphology of the 2D EBP material decreases the roughness coefficient to $R_a = 50–70$ µm. The considered methods for producing the 2D TiNi-based material allow the experimental samples to be created for the purposes of non-destructive testing.

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