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USE OF HYDROGEN HEAT TREATMENT IN THE PRODUCTION OF POROUS MATERIALS AND OBJECTS MADE FROM TITANIUM FIBER AND WIRE

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The possibility is investigated of improving mechanical properties of porous materials made from sintered titanium fibers and wire by hydrogen heat treatment. It is shown that the use of hydrogen heat treatment makes it possible to improve the strength of individually joined fibers and material as a whole. This makes it possible to prepare strong material with a high volume fraction of pores with a cross section of 100–500 μm and exhibiting good osteointegration capacity. This material is promising for preparing implants, replacing bone defects, or creating functional coatings on endoprosthesis elements.

***Keywords*:** *titanium, porous material, fiber, wire, implants, structure, properties, hydrogen heat treatment.*

Porous materials (PM) are used extensively in engineering and medicine. Various filter elements, heat-, noise-insulation, and damping materials are manufactured from them. The osteintegration properties of these materials are used in medicine, making it possible to reduce considerably the time for forming new bone tissue and to provide fixing implants to whose surface porous material is applied. Currently, PM are considered as a carrier with the use of cell technology. They are a carcase, within which specific cells are grown in a bioreactor for their subsequent placement in a human organism.

The base of a PM should provide good corrosion resistance in aggressive gas and liquid media, which they should clean, biological inertness towards organism tissues, exhibit a good set of mechanical properties, and these should be maintained in a porous condition. In addition, the pores themselves should have specific dimensions and volume fraction within material. Various materials are used (metals, polymers, ceramics) and technology (atomizing, sintering, self-propagating synthesis, etc.) in order to provide this extensive set of properties. Each of these materials and technologies display their own advantages and disadvantages, which gives rise to their selection in relation to a specific purpose.

Some of the most promising materials for a PM base are titanium and its alloys, which are used extensively in the chemical industry and medicine as corrosion-resistant and biologically inert materials. This quality it is quite different from stainless steels, cobalt alloys, and with respect to specific strength and cost it surpasses alloys based on precious metals, niobium, tantalum, etc. Compared with ceramic materials, PM based on titanium exhibit good ductility, impact strength, and also a more extensive production capacity for forming objects and its joints with other structural elements.

The formation of PM from titanium and its alloys is possible by plasma atomizing, sintering granules or powders, self-propagating high-temperature synthesis (for titanium intermetallics, for example, titanium nickelide), and electric-arc or

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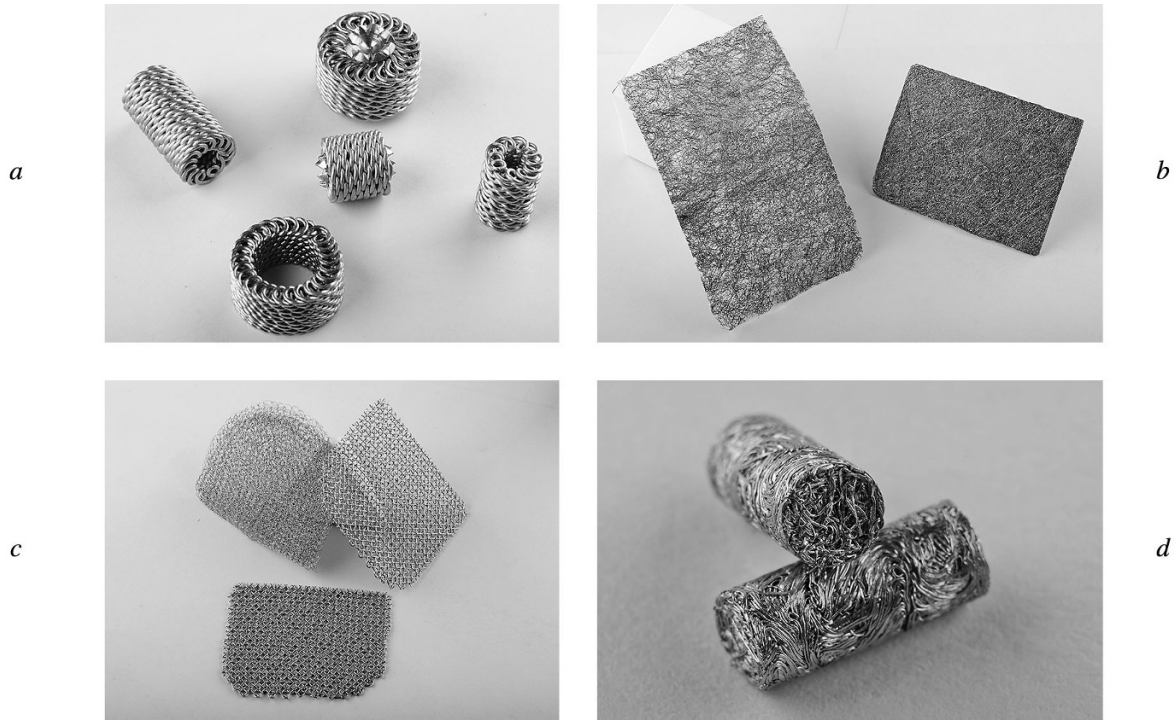

Fig. 1. Versions of using alloy VT1-00 porous materials: *a*) prostheses of vertebrae bodies made from wire 1.2 mm in diameter; *b*) cellular material made from wire 0.4 mm in diameter; *c*) sheet made of fibers with a cross section of 20 μm; *d*) cylindrical specimens made from wires 0.4 mm in diameter.

laser welding with layer-by-layer object formation [1, 2]. Of these technologies, SH-synthesis is used in a limited fashion, since incompletely reacted material has lower corrosion resistance and material biological inertness. For other technologies, the problem is provision of quite a good set of mechanical properties with considerable volume of material porosity. This is connected with the fact that the mechanical properties of titanium and its alloys are very sensitive to structure, and as a rule for their optimization significant deformation is used, which cannot be implemented with retention of volumetric porosity.

At the same time, hydrogen heat treatment (HHT) of titanium alloys developed in the last thirty years [3, 4] is a powerful production factor making it possible to convert the structure of titanium alloys without applying deformation and changing an object or semifinished product shape. HHT is used successfully for forming structures with both improved strength and fatigue properties for shaped castings [5], an improvement in deformation capacity of semifinished products, and formation within them of a sub-microcrystalline structure [6–10], etc.

Possibilities are considered in this work for using HHT in order to improve a set of PM mechanical properties, prepared by sintering wire or fiber from technically pure titanium. The choice of semifinished product for starting material was primarily determined by the use of PM developed in medicine. One of the main requirements for these materials is high pore volume fraction (70–90%) with dimensions of 100–500 μm. This is connected with provision of their osteointegration properties for intergrowth of osteoblasts with an average transverse size of 150–250 μm. In contrast to granules, it is possible to prepare specimens from fibers over a wide range of volumetric porosity, and by varying the size of the their cross section to provide a specified pore size. In addition, a PM fibrous structure makes it possible to reduce the probability of material breakage in compression and/or tension compared with granules or PM powders.

The starting raw material used for PM manufacture was wire of alloy VT1-00 0.2–1.2 mm in diameter and fibers with an average cross section of 10–50 μm, prepared by high-speed alloy melt solidification [11]. Porous specimens were formed from wires in the form of cylinders and fabric. Cylindrical specimens were prepared in the form of wound spirals, whose turns were heaped up, rolled, and twisted into a spiral of considerable diameter (Fig. 1*a*) [12], and cloth was prepared

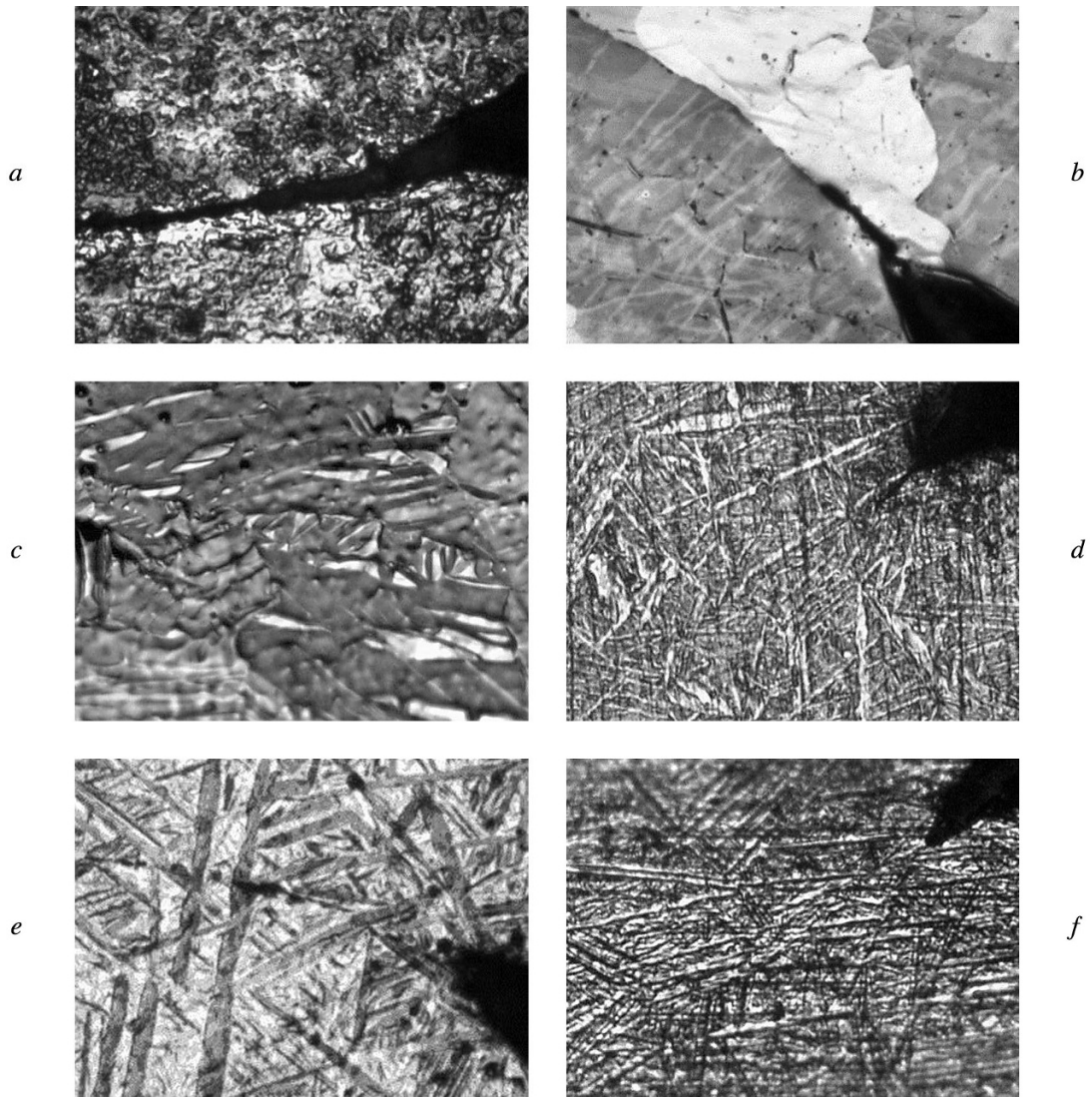

Fig. 2. Microstructure of wire specimen contact areas after sintering at 820 (*a*, *b*), 870 (*c*, *d*), and 920ºC (*e*, *f*) and hydrogen heat treatment (*b*, *d*, *f*), ×350.

by satin interweaving. Fragments of cloth were built up in layers in order that the wire direction in adjacent layers was arranged at an angle of 45º (see Fig. 1*b*). Cylindrical and flat specimens of fibers were prepared by pressing in dies of the required cross section (Fig. 1*c*, *d*). Workpieces prepared by different methods were sintered under load providing a pressure of 0.1–5 MPa at 800–960ºC. Sintered workpieces were given HHT, including hydrogenation at 800ºC, prior degassing at the same or lower temperature, and final vacuum annealing in the range 600–800ºC for 1–4 h.

The specimens prepared in this way were studied using metallographic analysis, and mechanical properties were measured. Study of sintered workpiece structure and properties showed that physical contact formed between wires or fibers occurs at above 900ºC. With a lower sintering temperature, contact is physical in nature with clear contact boundaries (Fig. 2*a*). The strength of these contacts is very low, and increases with an increase in sintering temperature in the β-region, and the specific proportion of physical contact (Fig. 2*b* and *c*). HTT was used in order to improve the strength of fiber contacts and PM as a whole. The principles of selecting this treatment regime may be formulated as follows:

1) temperature-concentration conditions for hydrogenation should provide conditions for complete $\alpha \rightarrow \beta$ phase recrystallization;

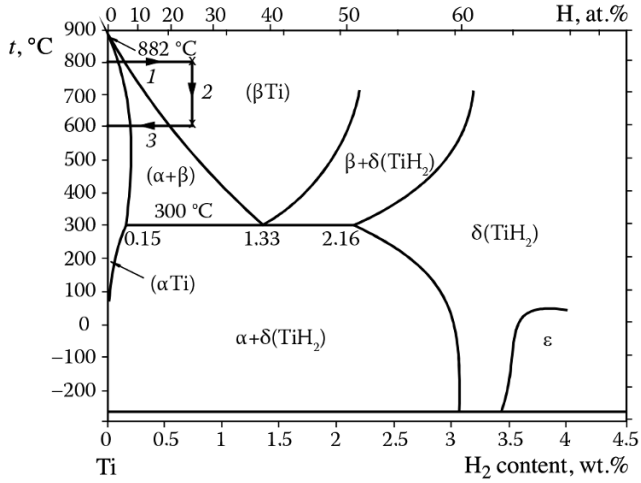

Fig. 3. Composition diagram for the Ti–H system [7] and HHT regime selection.

2) the hydrogenation temperature should be as low as possible in order not to lead to growth of β-grains during transition in a single-phase region;

3) the volumetric effect of $(\alpha + \beta) \leftrightarrow \beta$ transformation with introduction of hydrogen and degassing should be sufficiently high in order to provide phase work hardening and conditions for developing α- and β-phase recrystallization;

4) it is undesirable to use recrystallization connected with hydride formation, since this may lead to the formation of microcracks within material.

A choice was made for HHT regimes in accordance with these principles and the composition diagram for the Ti–H system (Fig. 3) [7]. The hydrogenation temperature (see Fig. 3, line *1*) was limited to 800ºC. At this temperature, the alloy with an original hydrogen content is represented solely by α-phase, and with an increase in its concentration there is $\alpha \rightarrow \beta$-transformation within the alloy. With a hydrogen content above 0.2%, the alloy is converted into a single phase condition. A temperature of 800ºC is insufficiently high for developing rapid β-grain growth.

In the next stage, two treatment versions are possible: cooling of hydrogenated alloy to normal temperature followed by vacuum annealing; degassing at 800ºC or somewhat lower temperature.

In the case of the first version during titanium alloy cooling it is possible to develop $\beta \rightarrow \delta$ and $\beta \rightarrow \alpha + \delta$ transformations within it, during which there is rapid phase work hardening due to the considerable difference in atomic volumes of coexisting phases. However, hydride formation may lead to the development of microcracks within the material structure, which under the action of thermal or other stresses will develop into macrocracks and lead to "self-propagating" failure of workpieces or objects. Therefore, the second version may be considered preferable with whose implementation as there is a reduction in hydrogen concentration $\beta \rightarrow \alpha$ transformation develops, causing additional phase work hardening. It is possible to reduce the temperature during dehydrogenation (see Fig. 3, line *2*), but not below the temperature limit for separation of secondary hydride and eutectoid transformation. In order to provide the formation of fine α-phase particles, it is desirable to remove hydrogen at 550–650ºC (see Fig. 3, line *3*). At this temperature, the original hydrogen concentration should provide a single-phase β-condition (i.e., the material should be hydrogenated to a concentration greater than 0.6% H_2), and after dehydrogenation only α-phase. Since under these conditions total dehydrogenation cannot occur, then workpieces and objects should be given additional vacuum annealing at 650–700ºC for 4 h. This annealing may be performed in normal vacuum furnaces with a considerable charge weight. This increases the economic nature of the whole process, since it will minimize the time of the working cycle for specialized dehydrogenation equipment and make it possible to provide safe (from the point of view of possible development of hydrogen brittleness) hydrogen content in finished objects.

In accordance with the above mentioned production principles, sintered workpieces were hydrogenated at 800ºC to a concentration of 0.8 wt.% H_2, after half an hour exposure the temperature was reduced to 600ºC, and hydrogen was pumped

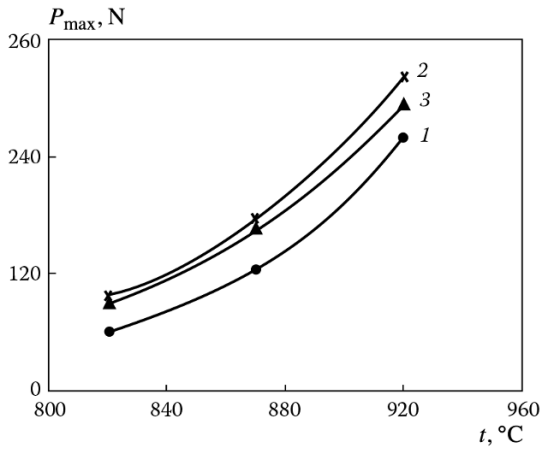

Fig. 4. Dependence of breaking force for cruciform specimens of alloy VT1-00 wire on sintering temperature: *1*) after sintering; *2*) after additional hydrogen heat treatment with vacuum annealing at 600ºC (*2*) and 800ºC (*3*).

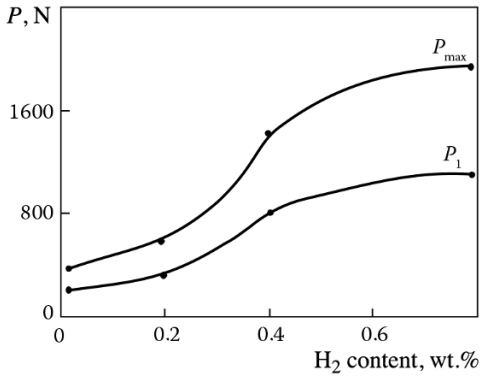

Fig. 5. Effect of hydrogen concentration during hydrogen heat treatment on maximum (P_{max}) and first (P_1) contact breaking force for an alloy VT1-0 wire joint in porous material.

from the workspace for 0.5 h. After this, workpieces were cooled to normal temperature and vacuum annealed at 600ºC for 4 h or 800ºC for 1 h.

In the first series of experiments, wire specimens 1.2 mm in diameter of alloy VT1-00 were used. Sections of wire were laid crosswise on each other and sintered with a steady increase in load to 10 N. After this, some specimens were given HHT and microstructural analysis for joint areas. Mechanical tests in shear were accomplished with determination of wire joint breaking force during pulling a cross-shaped specimen through a die with an opening 3 mm in diameter. In some cases under load there was separation of one of the wires to its contact boundary.

These tests showed (Fig. 4) that with a low sintering temperature (820ºC) the contact area is small, and its boundary is a mechanical joint without forming common grains (see Fig. 2*a*). The breaking force for this joint dos not exceed 60 N. As sintering temperature increases, there is an increase in contact area, common grains appear for two wire specimens, and the breaking force reaches 250 N after sintering at 920ºC. However, the material's structure changes, i.e., there is coarsening of β-transformed grains, and α-phase is represented by coarse platelets (see Fig. 2*e*).

Hydrogen heat treatment makes it possible to increase considerably the breaking force for specimens (up to 340 N), and this occurs in many cases not through the contact area, but through the main material. Within the microstructure of a

wire contact sintered at 870ºC and above, common grains form, and previous grains are not revealed in the microstructure. It should also be noted that after sintering at 920ºC during hydrogen heat treatment coarse α-platelets become significantly finer, particularly with a low (600ºC) temperature for final vacuum annealing. This leads to strengthening not only of the contact area, but for the main material as a whole.

In order to verify the efficiency of using hydrogen heat treatment for specimens of medicinal objects based on porous material made from alloy VT1-00 wire, an experiment was performed within which an endoprosthesis of a vertebra was tested in shear. With a record of the force from test unit grip movement a series of peaks was recorded, specifying the breaking force of individual wire contacts within the cross section of a cylindrical specimen (Fig. 1*a*). The change in force is shown in Fig. 5, relating to the first peak (P_1) and the maximum value of force in the specimens loading cycle (P_{max}) in relation to hydrogen concentration introduced during hydrogen heat treatment. A rapid increase was established in P_1 and P_{max} with an increase in hydrogen concentration to 0.4%, and more smoothly from 0.4 to 0.8%. It should be noted that within specimens given HHT there is a sharp increase in the number of peaks on the stress curve. This points to an increase in the number of contacts of physical and not mechanical nature. For specimens not given HHT the number of loading peak does exceed 100, but after HHT using 0.8% H_2 their number increased to 340. Using integration with respect to load of all the contact breaking forces, it is possible to talk about an increase in specimen breaking energy following HHT by a factor of 4.5 compared with a specimen without HHT.

Thus, use of hydrogen heat treatment makes it possible to increase considerably the strength of sintered porous material made from titanium base alloys.

Conclusion. These studies have shown that use of hydrogen heat treatment (HHT) makes it possible to improve the mechanical properties of sintered fiber porous materials (PM) made from titanium. A quite good set of PM mechanical properties may be achieved using sintering below the Ac_3 temperature, which makes it possible to retain the original material's fine-grained structure. This is an important factor, since it makes it possible to use the process for PM preparation in order to create porous coatings on implants. In this case, it is important that the treatment process occurs at a temperature below 900ºC in order not to worsen the structure of an implant and retain its mechanical properties.

Use of hydrogen heat treatment makes it possible not only to reduce the temperature, but also pressure during sintering. This provides PM preparation with the maximum possible volumetric porosity (80–90%).

Use in PM preparation of titanium fibers or wires of different cross section provides a possibility for varying pore size over a wide range, including in the range 100–500 μm in order to provide good osteointegration capacity of the material. The presence within the limits of one fiber or section of wires of numerous physical contacts with other material elements reduces the risk of PM particles breaking away, and provides good reliability of its use as an implant material in covering bone defects.

Analysis of the results obtained makes it possible to propose that HHT may be used effectively for improving the structure and increasing mechanical properties of porous material prepared not only by sintering granules and fibers, but also additive technologies, in particular a 3D-prototype using electron beam or laser welding of titanium powder and its alloys [13–15].

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