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The Effect of Severe Deformation on the Structure and Mechanical Properties of Titanium Hydride

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The effect of both deformation conditions and pressing pressure on the structure and properties of titanium hydride formed by various methods, such as quasi-hydrostatic pressing in a high-pressure chamber, free upsetting and static one-stage pressing with subsequent second compaction, is studied. As found out, the stresses exceeding the ultimate strength of titanium hydride appear at the contact surfaces of particles at high pressures. The consolidation of the powder occurs through the mechanism of particle crushing, which contributes to the further compaction of TiH_2 powder, and due to plastic deformation. As also found out, the deformation of titanium hydride under conditions of free radial shear provides plastic deformation at significantly lower pressures as compared to the uniform quasi-hydrostatic compression. As shown, the rate of hydrogen release from sintered compacts decreases at higher pressing pressure and the degree of deformation.

Key words: titanium hydride, severe deformation, pressing, quasi-

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hydrostatic compression, free upsetting, porosity, dehydrogenation rate.

Досліджено вплив умов деформування та тиску пресування на структуру та властивості гідриду Титану, сформованого різними методами, такими як квазигідростатичне пресування у камері високого тиску, вільний осад і статичне одностадійне пресування з подальшим повторним пресуванням. Встановлено, що на контактних поверхнях частинок за високих тисків виникають напруження, що перевищують межу міцности гідриду Титану. Консолідація порошку відбувається за рахунок механізму подрібнення частинок, що сприяє подальшому ущільненню порошку TiH_2, та за рахунок пластичної деформації. Також встановлено, що деформація гідриду Титану в умовах вільного радіяльного зсуву забезпечує пластичну деформацію за значно нижчих тисків порівняно з рівномірним квазигідростатичним стисненням. Показано, що швидкість виділення водню зі спечених компактів зменшується з підвищенням тиску пресування та ступеня деформації.

Ключові слова: гідрид Титану, сильна деформація, пресування, квазигідростатичне стиснення, вільний осад, пористість, швидкість дегідрування.

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1. INTRODUCTION

The rapid development of technologies constantly requires the use of materials with a unique combination of properties, namely high values of strength, hardness, thermal stability and, at the same time, low specific weight. One of the most promising materials is titanium, which, due to its properties, has become one of the most important construction materials today [1].

The use of titanium and its alloys in powder metallurgy allows solving a number of issues (high-energy consumption, high material losses, that result in high cost of products, *etc.*), which arise when parts are produced by traditional methods. However, the main obstacle to the widespread application of titanium powder metallurgy techniques into industrial production is the high price of powders and insufficient volume of their production. The price of titanium powders is significantly higher than the price of titanium sponge, and in some cases even higher than the price of ingots and some semi-finished products [2]. The main direction of the development of the titanium industry today is the expansion of the field of application of titanium and its alloys through the development of new economic technologies that provide a significant reduction in the cost of both the material itself and products from it in comparison with existing approaches [3, 4]. The use of titanium hydride instead of traditional titanium powder is more expedient both from the technical and economic point of view [5], since hydrogen activates the processes of consolidation of powders during sin-

tering, which provides a relative density of 98.5–99.5%, the required phase composition, microstructure, and chemical homogeneity with a low content of impurities [6]. However, the disadvantage of using titanium hydride in powder metallurgy technologies is its high brittleness, which negatively affects the compaction of powder particles at the stage of part formation. Nevertheless, it is known that the plasticity of titanium hydride increases after severe deformation; this is associated with increased mobility of dislocations [7, 8]. As known, the plastic deformation of hexagonal close-packed (h.c.p.) titanium is controlled by the sliding of screw dislocations [9].

The use of the techniques of severe deformation, including torsion under high pressure, equal-channel angular pressing, screw extrusion, free upsetting and forging [10–12] provides a non-trivial combination of strength and plasticity of powder materials. This becomes especially important for the formation of the structure and properties of brittle and low-plasticity materials, such as titanium hydride. The effect of increasing strength and plasticity after severe deformation at high pressures is known for many metallic materials, including titanium [13]; however, this effect has practically not been studied for titanium hydride. This determines the relevance and timeliness of researches on this issue. Therefore, the purpose of this work was to study the influence of pressing pressure and conditions of severe deformation on the structure and properties of titanium hydride formed by various methods.

2. EXPERIMENTAL TECHNIQUES

The initial titanium hydride powder was produced by hydrogenation of titanium sponge. Titanium hydride powder had an f.c.c. lattice with a hydrogen content of 4 wt.%. The powder was heterogeneous in the particle size in initial state. The size of the powder particles varied from 100 μm to several millimetres. Therefore, the powder was first ground in a titanium planetary mill, in the environment of ethyl alcohol, for 5 minutes. Grinding titanium hydride in a planetary mill increased the specific surface area of the powder, the density of structural defects in the crystal lattice, and decreased hydrogen content to 3.8 wt.% (determined by the method of reductive extraction with carbon in the flow of He with subsequent chromatographic registration of the reduction products); the chemical activity also increased [14]. After grinding, the < 50 μm powder fraction was sieved for further investigations. In order to study the deformation process and the effect of pressing pressure on the properties of the TiH_2 powder compacts, one-stage pressing in a steel split mold, second compaction, free upsetting between steel plates, and quasi-hydrostatic compression in a high-pressure chamber were carried out.

The fracture surfaces of the compacts were examined at a REM-106I

scanning electron microscope.

The phase composition was studied by x-ray analysis at a RIGAKU ULTIMA IV diffractometer with Cu$K_{\alpha_{1,2}}$ ($\lambda_{\mathrm{Cu}K_{\alpha 1}} = 0.1541$ nm) radiation.

The mechanical properties of the titanium hydride compacts were investigated by continuous indentation at a Micron-gamma unit [15]. The method of continuous indentation is based on automatic registration of the load on the indenter, as well as the depth of its penetration. The hardness and elastic modulus were determined by penetration curves according to Oliver W. C., Pharr G. [16] and international standard ISO/FDIS 14577-1:2002.

In order to study the kinetics of gas release from TiH_2, the compacts were heat treated at an ELA-6 electron-beam unit. The TiH_2 powder compacts were placed in a vacuum chamber with an electron gun. They were heated with a rate of 3–4°C/s up to 800°C with a directed and focused beam of accelerated electrons. The energy of the flow transformed into thermal energy; the material was heated due to the slowing-down of electrons in the material.

3. RESULTS AND DISCUSSIONS

The < 50 μm fraction of TiH_2 powder was examined at a high-resolution scanner (Innovative Sintering Technologies Ltd). The average size of the powder of this fraction was 7 μm. The particles of this fraction had irregular shape and varied in size (SEM, Fig. 1). The residual porosity of formed TiH_2 powder samples was determined (Table 1).

After one-stage pressing, the residual porosity was rather high (20%) that was associated with the features of the formation of brittle materials. Since titanium hydride is brittle, it has a completely different compaction mechanism compared to plastic titanium powder. Plastic titanium particles deform during pressing, forming comparatively large pores whose size decreases with increasing pressure. In contrast to this consolidation mechanism, brittle hydride particles crush and crumble under pressing, that leads to the formation of fine pores whose size practically does not depend on the applied pressure. Therefore, pressing of titanium hydride with additional second compaction of the compacts at a pressure of 800 MPa was investigated. The second compaction in a split mold is an effective way to reduce the porosity of powder materials [17]. After the second compaction, the residual porosity of the compacts was almost halved to 11–12%. The decreased porosity was caused by the elastic aftereffect. When the load was removed, the compacts increased in size; accordingly, the particles that were jammed during pressing split and slightly shifted, which contributed to a denser arrangement of titanium hydride particles in the compact [18]. However, taking into account the fact that the elastic

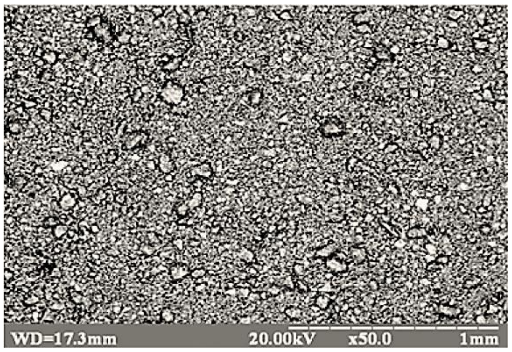

Fig. 1. Microstructure of TiH_2 after grinding in a planetary mill.

TABLE 1. Porosity of titanium hydride compacts formed by various methods.

Pressing method	Porosity, %
One-stage pressing (400 MPa)	19.37
Pressing with second compaction (800 MPa)	12.18
Pressing in high-pressure chamber (2.5 GPa)	2.47
Pressing in high-pressure chamber (4.2 GPa)	2.15
Pressing in high-pressure chamber (7.7 GPa)	1.91
Pressing with free upsetting (2.5 GPa)	1.22

aftereffect for low-plastic materials is rather insignificant, the shift of titanium hydride particles is not significant, which causes high residual porosity. Therefore, it is necessary to apply significantly higher loads that provide large deformations of 80–90%, which can be implemented in high-pressure chambers under conditions of quasi-hydrostatic compression or with free upsetting with radial shear.

Under pressing in a high-pressure chamber, stresses exceeding the ultimate strength appear on the contact surfaces of the particles. The particles crush, which contributes to the further densification of the TiH_2 powder and consolidation of the particles into solid compact (Figs. 2, *c*, *d*, *e*). This reduces the porosity of the compact to 1–2%.

After one-stage pressing, the particles were densely arranged on the fracture surface; brittle fracture on the surfaces of some particles was observed (Fig. 2, *a*). After pressing with second compaction, the number of crushed brittle particles increased significantly (Fig. 2, *b*); fine particles formed after crushing filled the pores between coarser particles, thereby increasing the density of the compact. After pressing in a high-pressure chamber, the consolidation of particles was observed; at a pressing pressure of 7.7 GPa, the particles combined into blocks. Ev-

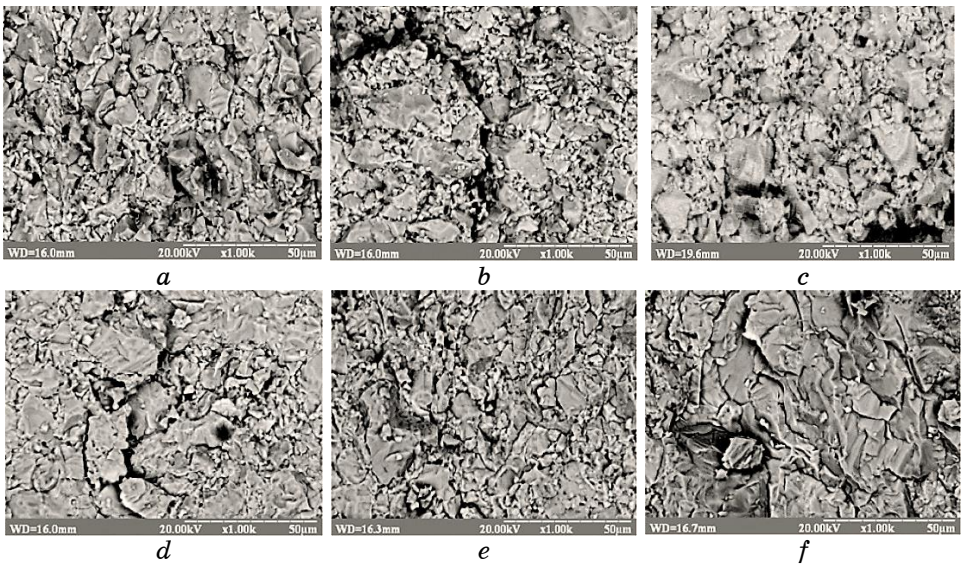

Fig. 2. Fracture surfaces of TiH_2 powder compacts formed by different methods: one-stage pressing (*a*); pressing with second compaction (*b*); free upsetting (*c*); pressing in high-pressure chamber at: 2.5 GPa (*d*), 4.2 GPa (*e*), 7.7 GPa (*f*).

idences of plastic deformation appeared, which was confirmed by some broadening of the x-ray diffraction peaks.

X-ray phase analysis showed that the compacts were in a single-phase state (titanium hydride) (Fig. 3). A comparative analysis of the

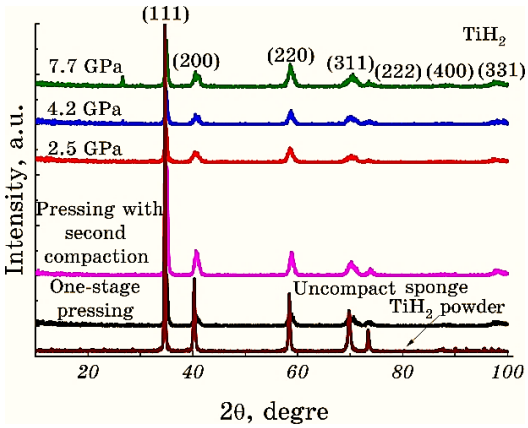

Fig. 3. X-ray diffraction patterns of TiH_2 compacts formed under different conditions: uncompacted sponge titanium hydride powder (*a*), one-stage pressing (*b*), pressing with second compaction (*c*), pressing in high-pressure chamber at 2.5, 4.2, and 7.7 GPa, respectively (*d*, *e*, *f*).

x-ray diffraction patterns showed that the pressing of titanium hydride powder does not affect the position of the diffraction peaks (*i.e.*, the lattice constant), which indicates the preservation of the hydrogen content in the material after processing with uniform compression. Without affecting the composition, the pressing of the titanium hydride powder led to a further broadening of the peaks (see Fig. 3), which indicates the development of plastic deformation during processing under conditions of quasi-hydrostatic compression.

An analysis of the profile of x-ray diffraction peaks of the original powder and compressed samples showed that their physical expansion was associated with the disturbance of lattice periodicity and microdeformations in the titanium hydride lattice caused by randomly distributed dislocations.

Along with the compaction under hydrostatic compression, the option of deformation of titanium hydride by free upsetting with large shear deformations was examined. Pressed compacts with an initial porosity of 19–20% were placed in annealed steel shell rings with a height of 14–15 mm (that corresponded to the height of the compacts) and an internal diameter of about 10 mm; then, they were placed between the steel plates of a press and compressed at a pressure of 2.5 GPa.

The degree of deformation of the compacts from titanium hydride under free upsetting was 80%. Comparatively brittle material did not crack or crush. Dense billets were produced with porosity not higher than 1–2%. The steel shell ring supported the compact, which prevented it from crushing during deformation. However, unlike the hardened plates of the press tool, the annealed steel shell ring was deformed together with the compact with a significant shift in the radial direction. Accordingly, the peripheral zone of the compact had significant shear deformations, unlike the central zone. The changes in the structural state in different zones of titanium hydride compacts after free upsetting were investigated.

The microhardness of the upset samples decreased from the periphery to the centre of the compact (3.5–5.0 and 1.8–2.0 GPa, respectively) (Fig. 4). This decrease in microhardness was accompanied by a decrease in the elastic modulus from 68.7 to 54.7 GPa (Table 2). At the same time, the ductility factor of titanium hydride naturally increased from 0.812 to 0.869, which can be explained by a higher density in the centre of the compact.

With the increase in hardness, the stresses on the periphery increased from 0.407 to 0.711 (Table 2) due to a more complicated deformation mechanism: a combination of normal and shear deformations, in contrast to the centre with only normal deformations.

The higher stresses on the periphery are also evidenced by structural changes in the material (see the results of x-ray structural analysis in Fig. 5).

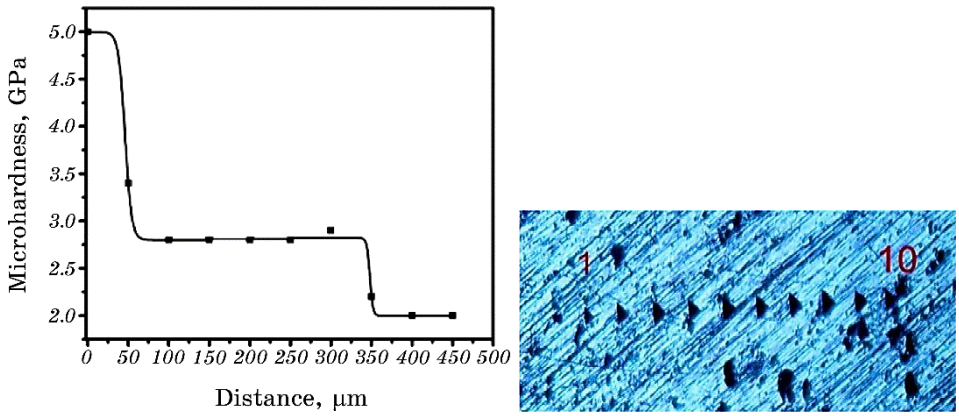

Fig. 4. Changes in microhardness of TiH_2 compact from periphery to centre after upsetting.

TABLE 2. Mechanical properties of titanium hydride compacts after free upsetting.

Zone	*H* (Meyer), GPa	*E*, GPa	Ductility factor	Stress, GPa
Periphery	3.51	68.7	0.812	0.711
Centre	1.86	54.7	0.869	0.407

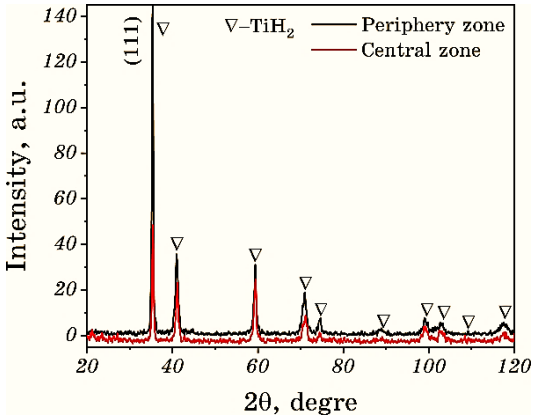

Fig. 5. X-ray diffraction patterns of titanium hydride after upsetting in central and peripheral zones.

The results of the x-ray phase analysis show that the (111) peak has higher intensity on the periphery (higher deformations) compared to the centre (lower deformations). This may be associated with the fact that titanium hydride has an f.c.c. lattice with main slip direction

{111}. In turn, the lattice constant in the centre of the sample was 4.4167 Å, whereas on the periphery it was 4.4131 Å, which indicates a greater degree of deformation during processing, as initially it was 4.4183 Å.

Thus, the process of free upsetting provides compaction of brittle powder materials to a non-porous state. The use of steel shell rings with a given level of plasticity provides conditions for producing billets with a gradient of properties across their cross-section. It should be noted that the deformation of titanium hydride under conditions of free radial shear provides plastic deformation at much lower pressures compared to the uniform quasi-hydrostatic compression.

In order to determine the rate of gas release from TiH_2 compacts, the samples pressed under different conditions were heat treated in an ELA-6 electron beam unit. The amount of hydrogen released during dehydrogenation decreased with the pressing pressure. This effect can be explained by Le Chatelier's principle. According to this principle, a system in stable equilibrium, when an external action is applied to it (change in temperature, pressure, *etc.*), tends to return to the state of equilibrium.

The dehydrogenation rates of TiH_2 samples compacted at different pressures are listed in Table 3.

Since the crystal lattice is deformed at high pressures, zones with high stresses appear in it. In the TiH_2 system, hydrogen atoms occupy mainly tetrahedral interstitial sites. Since the system tends to equilibrium and stress relaxation, some hydrogen atoms move into the octahedral interstitial nodes. These sites are smaller, so it takes more energy to release hydrogen from the sample. This effect leads to a decrease in the gas release rate at higher pressing pressures and deformations of the compacts. Upon pressing with subsequent second compaction, the gas release rate increases, because partial stress relaxation occurs, and hydrogen atoms remain in the tetrahedral interstitial sites after the

TABLE 3. Gas release rates for TiH_2 samples compacted at different pressures.

Type of deformation	One-stage pressing (400MPa)	Pressing with second compaction (800MPa)	Pressing in a high-pressure chamber (2.5GPa)	Pressing in a high-pressure chamber (4.2GPa)	Pressing in a high-pressure chamber (7.7GPa)	Free upsetting (2.5GPa)
Gas release rate, $Pa/s \cdot 10^{-2}$	0.10202	0.10853	0.08992	0.07844	0.03872	0.02456

first pressing.

The reduction of gas release at high pressures is also associated with almost complete closure of the pores in the compacts. The most intense pore closure occurs under shear deformations, *i.e.*, when a compact deforms in the radial direction.

4. CONCLUSIONS

The application of severe deformation to titanium hydride compacts by means of hydrostatic compression in a high-pressure chamber or free upsetting provides porosity reduction to 1–2%. This is caused by the deformation of the structure and formation of stresses that exceed the ultimate strength on the contact surfaces. According to fractographic investigations, some particles were crushed in the compacts formed by one-stage pressing and with second compaction, whereas at high pressures, consolidation of particles was observed, and signs of plastic deformation appeared, which was confirmed by the broadening of x-ray peaks.

The pressing of the titanium hydride powder did not lead to changes in the position of the diffraction peaks, *i.e.*, the lattice constant did not change, which indicates the preservation of the hydrogen content in the material after hydrostatic compression.

It is shown that free upsetting with radial shear allows producing compact titanium hydride billets where structural components vary depending on the deformation zone. A gradient of physical and mechanical properties of the compact material was observed after upsetting. Microhardness and elastic modulus decreased from 3.5–5.0 to 1.8–2.0 GPa, and from 68.7 to 54.7 GPa, respectively. The ductility factor increased from 0.812 (centre) to 0.869 (periphery).

The gas release rate of sintered samples decreased from $0.102 \cdot 10^{-2}$ Pa/s to $(0.024–0.038) \cdot 10^{-2}$ Pa/s with increasing pressure and degree of pressing deformation. This is due to the fact that hydrogen atoms initially located in the tetrahedral interstitial sites are pushed into octahedral ones at high pressures. This dependence was not observed for pressing and subsequent second compaction that is explained by partial stress relaxation after the first pressing.

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