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The Peculiarities of Structure Formation Upon Sintering of TiH$_2$+TiB$_2$ Powder Blends

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The investigation results on peculiarities of phase and structure formation as well as sintering kinetic of compacted TiH$_2$ - TiB$_2$ powder blends. It was shown, the most intensive shrinkage upon heating took place within temperature range of TiH$_2$ dehydrogenation (400 ÷ 650 ^{0}C). Heating of powder blend up to sintering temperature (1350 ^{0}C) resulted in formation of acicular TiB particles in titanium matrix, the amount of particles is increased with increase in exposure to 20 min. The longer duration of isothermal exposure did not lead to increase in amount and size growing of TiB particles. X-ray analysis of sintered TiH$_2$+TiB$_2$ powder blend demonstrated the presence of titanium matrix phase, orthorhombic TiB phase, and traces of Ti-B compounds of different concentrations (Ti$_3$B$_4$ and Ti$_2$B$_5$). The dilatometric investigations proved that addition of boride compounds and increase in boride content in powder blend led to decrease in shrinkage upon sintering as compared to shrinkage of single TiH$_2$ powder compacts.

Key words: titanium, boride, hydride, sintering, structure, powder, dehydrogenation, metal matrix composite, powder blend.

Introduction

Contemporary titanium-based alloys possess unique combination of properties, namely, low density as compared to that of steels and heat-resistant nickel alloys, high corrosion resistant, high specific strength within wide temperature range. These properties became critical and determine the advantage of titanium usage in such high-technology spheres as aerospace application, medicine, chemical and oil industries [1-4]. At the same time, the number of titanium alloys are characterized with relatively low tribotechnical properties. These properties can be improved by creation of metal matrix composites strengthened with high modulus compounds such as titanium carbides, borides and silicides, SiC, etc [5-7]. The manufacturing technologies for such composites are mainly based on powder metallurgy approach [8-10].

An effective approach to obtain sintered titanium-based materials is use of titanium hydride TiH$_2$ powder instead of conventional metal titanium powder. Such substitution provides considerable activation of diffusion upon sintering and gives the opportunity to purify the material owing to action of atomic hydrogen evolved from crystal lattice of titanium hydride on vacuum heating [11, 12]. Due to hydrogen effect on the material, the unique structural conditions of sintered titanium alloys possessing high physics and mechanical properties are formed. Also, the use of TiH$_2$ as raw material leads to cost-efficiency, because of titanium hydride is cheaper than conventional titanium powders produced with hydrogenation/dehydrogenation approach.

Preliminary investigations of authors revealed that
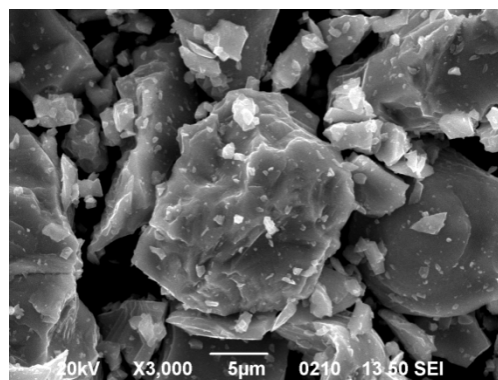
Fig. 1. Titaniumhydridepowderused for preparation of powder blends.

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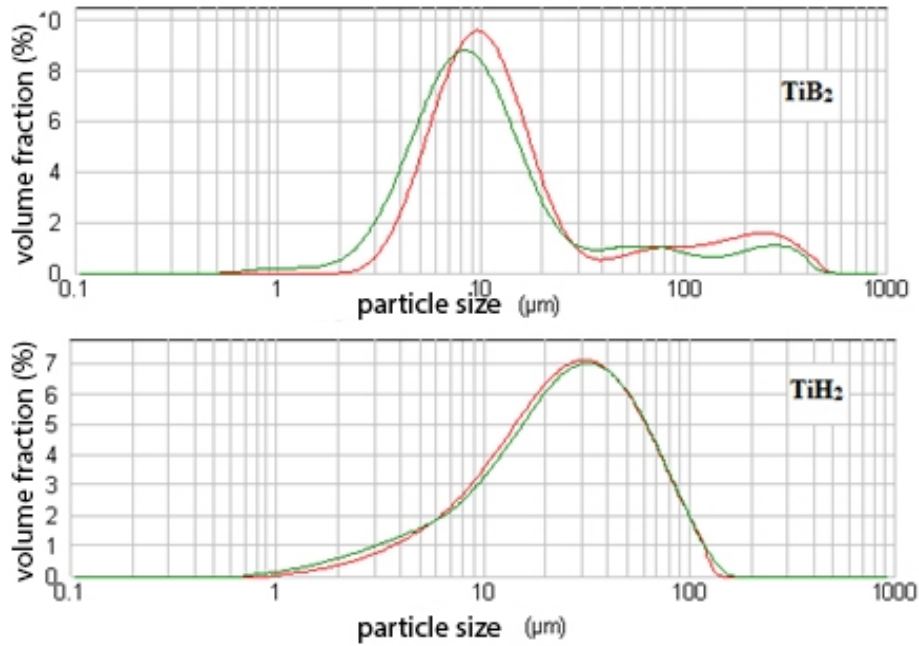
Fig. 2. Size distribution of powders used in present study:1 – initial powders, 2 – powders after ultrasonic treatment.

sintering of powder blends on the base of titanium hydride allows creation of metal matrix composites strengthened with various particles. The most perspective results in the sense of obtaining of microstructure uniformity and reduced porosity were achieved for titanium composites strengthened with TiB particles, which were produced by sintering of TiH_2 +TiB_2 powder blends.

The aimof present investigation was to establish the main regularities of structure and phase composition evolution on sintering of TiH_2+TiB_2 powder blends to formtitanium-based composite material strengthened with TiB particles.

I. Materials and Experimental Procedure

Hydrogenated titanium powder (size of particles less than 100 μm, Fig .1) was used as the base one for preparation of powder blends. Hydrogen content in the powder and its phase composition corresponded to single-phase titanium hydride TiH_2. The particle size distribution of powders under investigation was determined with Malvern Mastersizer 2000E analyzer. To evaluate the opportunity of powder particle coagulation, the particle size was measured in initial state as well as with ultrasonic treatment.

The boron was added as titanium diboride TiB_2 powder to titanium hydride one. Titanium diboride particles are actively reacted with titanium matrix at elevated temperatures following reaction $TiB_2 + Ti = 2TiB$ which lead to formation of TiB particles.

Starting powder blends based on titanium hydride with addition of 5÷20 mass.% TiB_2 were prepared in roll blender. Blends were compacted in steel die at 650 MPa in cylindrical specimens 10 mm in diameter, 10-12 mm

in height. Vacuum sintering of specimens was performed at 1350 ^{0}C with different durations of isothermal exposure: 1 min to 5 hours. Heating rate to sintering temperature was 10 ^{0}C/min, after sintering specimens were cooled in furnace.

The density and porosity of compacted and sintered specimens were determined with Archimede`s technique. Microstructure investigations were performed using light microscopy (Olympus GX71) and scanning microscopy (REM 106 I). The investigation of physical processes upon heating of powder compacts was performed using high-temperature vacuum dilatometer [14]. The phase composition was determined by X-ray analysis using DRON-3M diffractometer with CoKα irradiation.
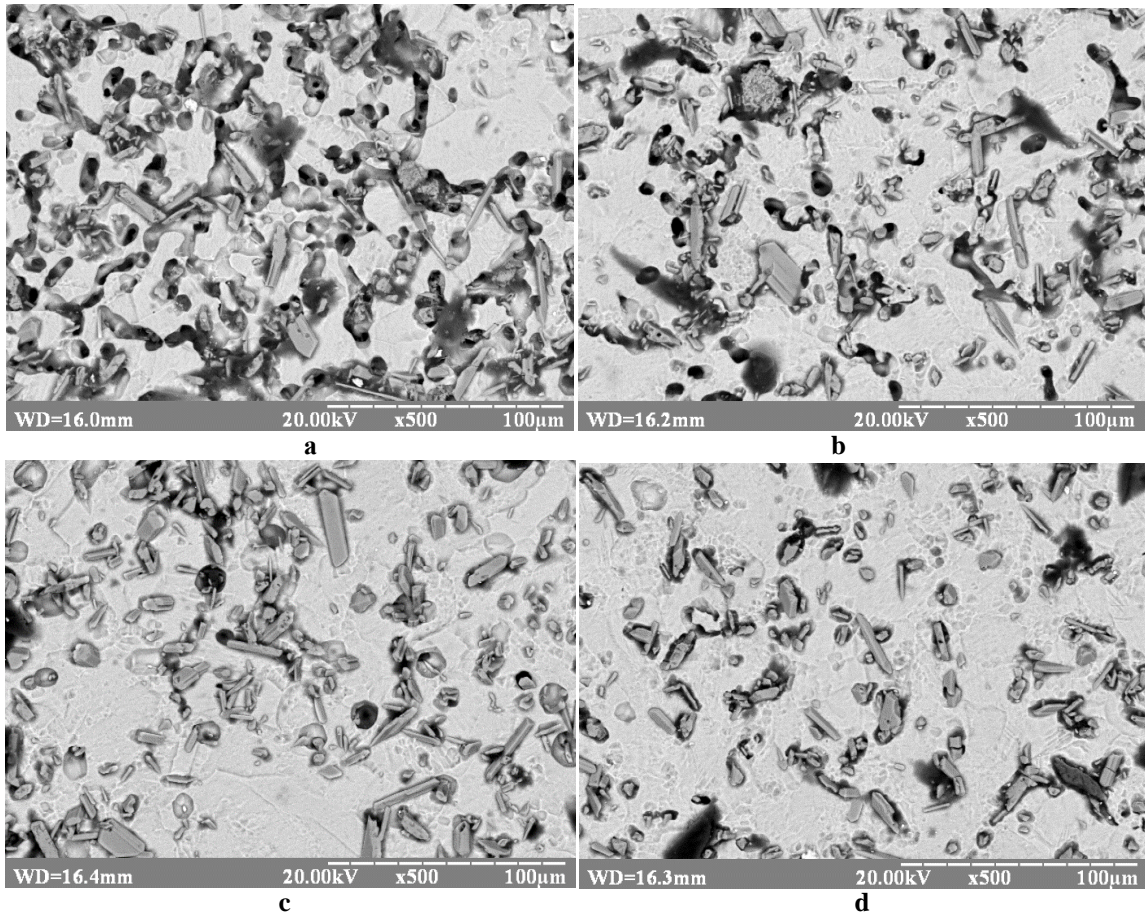
II. Results and Discussion

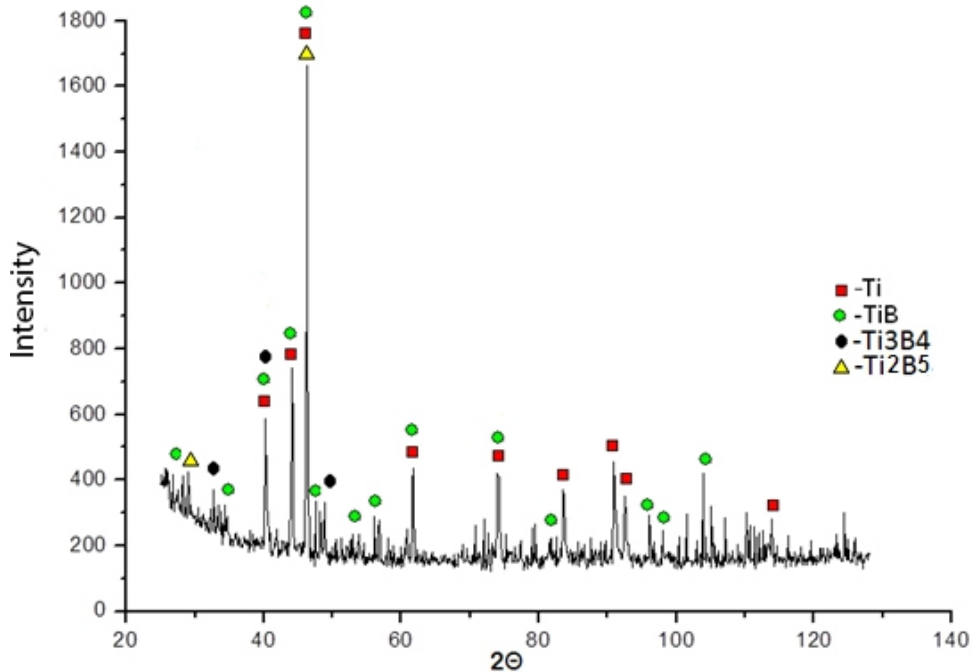Particle size distributions of initial powders are shown on Fig. 2. The average size of TiB_2 particles is not
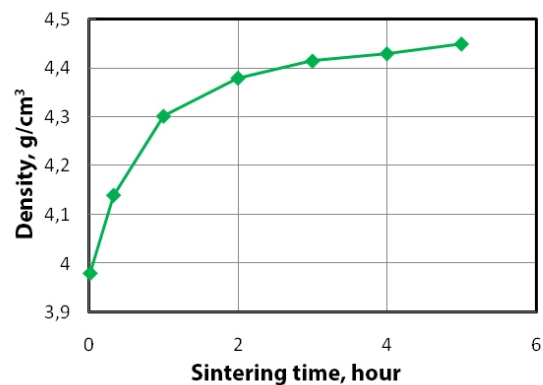
Fig. 3. Dependence of density for TiH_2 + 5 % TiB_2compacts on duration of isothermal exposure at 1350 ^{0}C.

Fig. 4.SEM images of TiH$_2$ + 5 %TiB$_2$ sample microstructure after exposure at 1350 ^{0}C: a - 1 min.;
b - 20 min.; c – 60 min., d - 300 min.

Fig. 5. X-ray diffraction pattern of composite produced by sintering of TiH$_2$ + 5 % TiB$_2$ powder blend at 1350 ^{0}C.

more than 10 μm while peak of TiH$_2$ powder distribution curve is around of 30-40 μm. Ultrasonic treatment of powders shifts size distribution peak for TiB$_2$ powder towards lower size values (Fig 2, a), while for titanium hydride powder the influence of ultrasonic treatment is not appeared (Fig. 2, b).

Investigation of sintering kinetic for TiH$_2$ + 5 % TiB$_2$ compacts revealed growth of their density upon heating within 400-800 ^{0}C range due to dehydrogenation of titanium hydride and development of δ-TiH$_2$→β-Ti →α-Ti phase transformation. At temperatures above 800 ^{0}C the matrix phase consists of completely dehydrogenated

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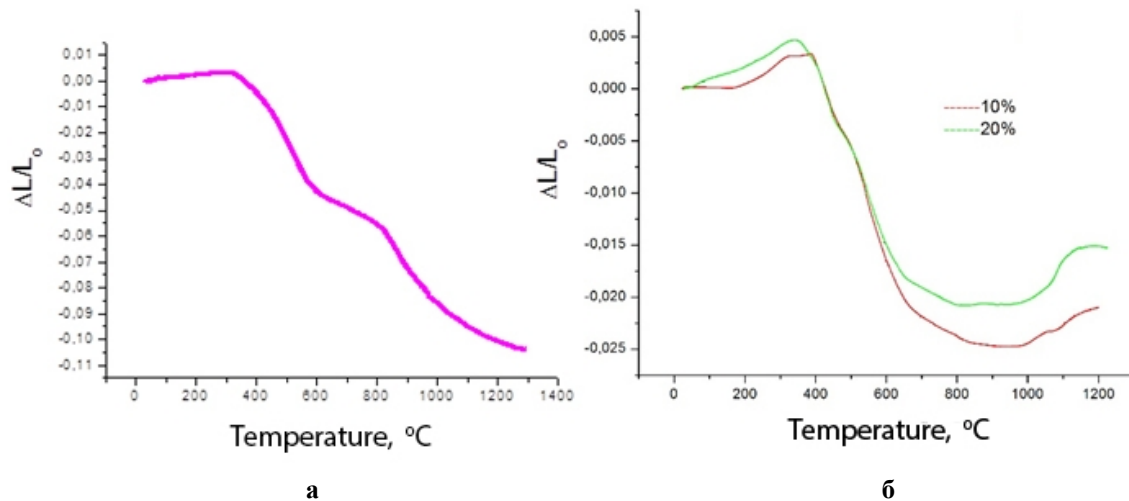**Fig. 6.** Dilatometric heating curves for TiH_2 (a) and blends of TiH_2 + (10 and 20 %) TiB_2 (b).

titanium particles.

Evaluation of influence of isothermal exposure duration at 1350 ^{0}C on material density had shown (Fig. 3) the most active shrinkage of compact during beginning 1-2 hours of isothermal exposure. This result is due to diffusion activation because of increase in amount of crystal lattice defects upon noted phase transformation and hydrogen emission. At sintering temperature (1350 ^{o}C) when titanium matrix is in single-phase β condition, the density growth is gradually slowed down after 2 hours exposure and became closer to theoretical density value.

The analysis of microstructure evolution upon isothermal exposure shows that TiB_2 particles in powder blend are not stable. Interaction following reaction $TiB_2+Ti\rightarrow2TiB$ results in formation of TiB particles which amount and composition are determined by duration of high-temperature exposure.

Microstructure evolution involves sintering of titanium particles and development of above noted reaction with dissolution of TiB_2 particles, nucleation and growth of TiB particles. It can be seen (Fig. 4,a), acicular TiB particles are formed in titanium matrix already during heating to 1350°C and 1 min holding at this temperature. Increase in sintering time up to 20 min leads to density growth (Fig. 3) due to sintering of titanium particles and simultaneous increase in amount of TiB needles (Fig.4,b). During further increase in time of isothermal exposure, the amount of TiB needles and their size remains nearly constant. Thus, during 1÷5 hours exposure microstructure evolution consists in sintering of the material (Fig. 4, c, d) and density growth up to 4,45 g/cm^3 after5 hours (Fig. 3).

X-ray diffraction pattern of sintered TiH_2+TiB_2 samples (Fig. 5) confirms titanium matrix as main phase and presence of orthorhombic TiB phase as well as traces of Ti-B compounds of other concentrations (Ti_3B_4 and Ti_2B_5). At the same time, initial TiH_2 and TiB_2 phases are not detected for sintered specimens.

For more detailed investigation of kinetic of monoboride TiB formation upon heating, the dilatometric study of single titanium hydride and powder blends of TiH_2 with additions of 10÷20 % TiB_2 has been performed. Compositions with increased TiB_2 content

were used for better demonstration of thermal effects upon heating of specimens.

It is seen from dilatometric study (Fig. 6), the minor thermal expansion of powder compacts takes place within 300÷350 ^{0}C for all samples including single TiH_2 (Fig. 6,a) and blends on its base with titanium diboride additions (Fig. 6,b). Further intensive shrinkage related to dehydrogenation of titanium hydride, this process is completed of about 600÷650 ^{0}C for all blends under investigation. At the same time, shrinkage value at this stage of heating depends on TiB_2 amount in powder blend. Increase in TiB_2 content with corresponding decrease in titanium hydride content results in decrease in shrinkage from ~5 % (single TiH_2 , Fig. 6,a) to 2,3÷1,8 % (blends with 10÷20 % TiB_2 , Fig. 6,b).

It should be emphasized, for both single titanium hydride and its blends with TiB_2 powder the most significant shrinkage is observed within 400÷650 ^{0}C range which corresponds to intensive dehydrogenation. The shrinkage rate is reduced within 600÷850 ^{0}C range. After dehydrogenation is completed (temperature range above 800 ^{0}C), activation of diffusion again leads to acceleration of shrinkage of samples without TiB_2, and linear shrinkage reach about of 10% at 1200 ^{0}C (Fig 6,a). However, presence of TiB_2 in powder blends results in retardation of shrinkage at 800÷1000 ^{0}C, and noticeable swelling of compacts on further heating from 900-1000 to 1200 ^{0}C(Fig. 6,б). So, linear shrinkage of compacts containing TiB_2 upon reaching sintering temperature is considerably lower (not more than 1.5÷2 %) than for compacted single TiH_2, (~10 %). The higher is content of boride phase in titanium matrix the lower is shrinkage of corresponding compacts.

The above described effect obviously caused by reaction between TiB_2 particles and titanium matrix, which resulted in dissolution of initial TiB_2 particles in titanium and simultaneous formation of monoboride TiB phase as needle precipitation in the matrix.

The theoretical calculations give ~11 % decrease in volume of boride phase because of $TiB_2+Ti=2TiB$ reaction. However, the fact that volume of compact is conversely increased at 1000-1200 ^{0}C (Fig. 6,b) can be explained by pore formation. Since diffusivity of titanium in boron is negligibly lower than diffusivity of

boron in titanium [15], one-way migration of boron atoms into titanium matrix is realized upon sintering causing formation of acicular TiB particles, while vacancy stream in opposite direction forms secondary pores (Kirkendall`s porosity).

At the same time, authors of study [16] believe the mechanism of pore formation upon sintering of TiB_2+Ti systems is caused mainly by limited plasticity in local volumes of titanium matrix at interface boundaries between matrix and acicular TiB particles which length is increased at temperature rise.

Basing on data [16], the monotonous growth of linear size of $Ti+TiB_2$ powder compacts was observed upon heating up to ~840 ÷ 910 ^{0}C for samples with 5-10 % (vol.) TiB and up to 1185 ^{0}C for samples with 20 % (vol.) TiB. Contrary, our data for titanium hydride based compacts demonstrate similar dependency up to ~400 ^{0}C only, while at higher temperatures minor shrinkage is observed. This result can be explained by significant activation of diffusion processes upon sintering owing to influence of atomic hydrogen evolved from material, namely, increase in amount of crystal lattice defects due to phase transformations upon dehydrogenation.

Conclusions

1. The investigation of sintering of compacted TiH_2 + 5 % (mass.) TiB_2 powder blend showed the growth of compact density already upon heating stage within 400-800 ^{0}C range together with dehydrogenation of base powder. Isothermal sintering at 1350 ^{0}C led to noticeable shrinkage during first 1-2 hours, then density growth is gradually retarded becoming close to theoretical value.

2. Heating of TiH_2 + TiB_2 powder blends resulted in formation of acicular monoboride particles in titanium matrix. Increase in sintering duration to 20 min is accompanied with increase in amount of TiB needles, while longer sintering did not lead to further growth of amount and size of TiB needles.

3. X-ray analysis of sintered TiH_2+TiB_2 compacts reveals α-Ti as the base matrix phase, orthorombic TiB phase and traces of titanium-boron compounds of other concentrations (Ti_3B_4 and Ti_2B_5). Starting TiH_2 and TiB_2 phases does not present in the sintered material.

4. Dilatometric studies demonstrate noticeably lower linear shrinkage of titanium hydride compacts with TiB_2 additions (not more than 1.5-2%) as compared to that for titanium hydride compacts without borides (~10 %). The higher is content of boride phase in titanium matrix the lower is shrinkage upon sintering of compacts.

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Особливості структуроутворення при спіканні порошкових сумішей системи TiH₂+TiB₂

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В роботі наведені результати досліджень особливостей фазо- та структуроутворення та кінетики спікання пресовок з порошкових сумішей системи $TiH_2 - TiB_2$. Показано, що найбільш інтенсивна усадка при нагріві відбувається в температурному інтервалі дегідрування TiH_2 ($400 \div 650\ ^0C$). Нагрів порошкової суміші до температури спікання ($1350\ ^0C$) призводить до утворення в титановій матриці голкоподібних частинок монобориду титану, вміст яких в структурі підвищується із збільшенням часу витримки до 20 хв. При подальшому збільшенні часу ізотермічної витримки кількість голок монобориду титану залишається практично сталою без помітної зміни їх розмірів. Рентгенофазовий аналіз спечених зразків із суміші TiH_2+TiB_2 вказує на наявність у сплаві основної матричної фази титану, ліній фази TiB з орторомбічною граткою, та слідів сполук титану з бором іншої концентрації (Ti_3B_4 та Ti_2B_5). Результати дилатометричних досліджень показали, що введення в склад шихти боридних сполук та збільшення їх вмісту в шихті призводить до помітного зменшення усадки в процесі спікання по відношенню до усадки пресовок із порошку гідриду титану без боридних фаз.

Ключові слова: титан, борид, гідрид, спікання, структура, порошок, дегідрування, металоматричний композит, шихта.