Role of Hydrogen and Alloying Elements in Titanium Hydride Based BEPM of Titanium Alloys

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The blended elemental powder metallurgy (BEPM) approach based on titanium hydride powder generally results in a better balance of the mechanical properties of the processed alloys in comparison to the properties of the alloys processed with common titanium powder. In this paper, the influence of hydrogen and various alloying elements on sintering behavior of the blends of titanium hydride and master alloys is analyzed. The final microstructure results from the competitive development of chemical homogenization, healing of porosity, and grain growth, which demonstrates specific features for each combination of the alloying elements. Experimental results were used to optimize the processing parameters for the CP-Ti and three alloys (Ti-6Al-4V, Ti-5Al-5V-5Mo-3Cr, Ti-10V-2Fe-3Al) so as to reach a desirable combination of homogeneous fine-grained microstructure and high relative density (low porosity) and, hence, a high balance of their mechanical properties.

Keywords: Titanium hydride, powder, hydrogen, diffusion, alloying elements

1. Introduction

The blended elemental powder metallurgy (BEPM) is successfully used for a cost-effective production of titanium alloys and components. In the traditional BEPM approach, the blends of titanium sponge fines and alloying powders are pressed and then transformed into the bulk homogeneous alloys upon vacuum heating. The attainment of desirable mechanical characteristics of BEPM produced titanium alloys is an important issue which determines the opportunities for their practical application. The desirable properties can be achieved even in the simplest BEPM press-and-sinter option when powder blends on the base of titanium hydride TiH₂ powder instead of common titanium powder are used. As compared to titanium powder, application of titanium hydride demonstrated a positive influence on the alloy synthesis process and final material characteristics. Atomic hydrogen dissolved in the titanium crystal lattice is evolved upon vacuum heating, affecting the material and resulting in improved density (up to 98-99% of the theoretical value) after pressureless sintering, desirable microstructure and admissible content of gas impurities in the final material and, hence, sufficient mechanical properties. The whole BEPM synthesis consists of chemical homogenization of heterogeneous powder compacts, their densification (pore healing) and microstructure evolution including grain growth, all these processes are controlled by diffusion. However, the specific features of the processes and final material characteristics considerably depend on total composition of an alloy produced. Achievement of sufficient density level of 98% is nonproblematic for Ti-6Al-4V composition, but is a challenging issue for near beta Ti-5553 and Ti-1023 alloys.

Despite the doubtless advantages of titanium hydride application in BEPM processing, a mechanism of the useful hydrogen effect has not been quite clear so far. Furthermore, since the density and microstructure peculiarities of synthesized titanium alloys depend on their compositions, the role of individual alloying elements and their combinations in formation of these characteristics has to be elucidated. The aim of present study was to clarify hydrogen and alloying element influence on densification, chemical homogenization, and microstructure evolution upon BEPM press-and-sinter processing. A better understanding of these matters will contribute to the achievement of a desirable combination of homogeneous fine-grained microstructure and high relative density (low porosity), which is necessary to attain a sufficient balance of mechanical properties of alloys produced.

2. Experimental Procedures

Titanium hydride TiH₂ powder (3.5 wt. % H, size of particles <100 µm, average particle size of 40 µm) was used as the base powder in present investigation. To clarify the role of hydrogen, a portion of TiH₂ powder was dehydrided to produce Ti powder of the same particle size distribution; both TiH₂ and Ti powders were comparatively used in press-and-sinter manufacturing of bulk CP-Ti. The Ti-6Al-4V (wt. %), Ti-5Al-5V-5Mo-3Cr (Ti-5553) and Ti-10V-2Fe-3Al (Ti-1023) alloys were produced from TiH₂-based powder blends with complex master alloy Al-V, Al-V-Mo-Cr and V-Fe-Al powders correspondingly. To reveal the influence of individual alloying elements on the densification features, binary Ti-10V, Ti-2Fe, and Ti-3Al compositions based on TiH₂ powder with Fe, V elemental powders and 66Ti-34Al master alloy powder were studied. Content of alloying elements in the binary compositions corresponded to Ti-1023 alloy. The size of all alloying powders was less than 63 µm.

BEPM processing included blending of powders, their compaction at room temperature at 640 MPa followed by synthesis in a vacuum furnace at 1250°C for 4 h. In all cases heating to 1250°C was performed with rate of 7°C/min, except specially noted experiments.
where higher heating rate was used.

The shrinkage behaviour of powder compacts was studied upon heating (7°C/min) in a dilatometer additionally equipped with a mass-spectrometer to analyse gas release from the compacts. Light microscopy, SEM, EDX microanalysis and in situ X-ray analysis upon heating, were employed for material characterization. Densities of compacts were measured with the Archimede’s technique. Tensile properties of the synthesized alloys were measured at room temperature following ASTM E8M-04 specification.

3. Results and Discussion

3.1 Hydrogen in CP-Ti Processing

The titanium hydride powder was compacted to a relatively low density of green samples (3.06 g/cm³) as compared to titanium powder (3.47 g/cm³). After sintering, vice versa, the CP-Ti samples produced from TiH₂ powder had a higher density (4.43 g/cm³, i.e. 98.2%) than those sintered from Ti powder (4.37 g/cm³, 97.0%). This result once more confirms the advantage of hydrogenated titanium to achieve higher sintered densities, the same as the results early obtained for Ti-6Al-4V composition. The mechanism of the hydrogen influence on sintered density becomes clear from an analysis of TiH₂ behavior upon compaction and heating processing stages, which determines final density.

Compacted TiH₂ powder demonstrated a lower green density as compared to Ti powder mainly due to the difference in densities of these bulk materials (3.8 g/cm³ and 4.51 g/cm³ correspondingly), while volume fractions of pores were nearly equal for both compacted powders. However, the TiH₂ and Ti compacts had different morphology of initial voids due to the differences in mechanical properties of these materials. Titanium hydride has a significantly lower strength (150-250 MPa) and a poor plasticity (not more than 3%) under compression as compared to titanium. Thus, a distinctive feature of brittle titanium hydride was the crushing of its particles into smaller edged fragments under compaction loading, Figure 1. The fragments which size was noticeably smaller than average size of starting TiH₂ particles, formed a specific network of fine (less than 10-15 µm) initial voids uniformly distributed over the compact. Contrary, non-fragmented Ti particles formed larger voids (up to 20-30 µm) in the green compacts. The smaller size of initial voids provided an opportunity for their easier disappearing upon further sintering, thus a benefit for TiH₂ powder appeared already at the compaction stage.

A characteristic feature of hydrogenated titanium is the existence of dehydrogenation process, i.e. hydrogen evolution from material and inherent significant shrinkage upon vacuum heating above 320°C, Figure 2. The temperature interval of dehydrogenation, and corresponding changes in the phase composition depend on a heating rate and a rate of hydrogen evacuation from heating chamber. Relatively slow (7°C/min) heating led to the TiH₂→β→α consequence of phase transformations and completion of dehydrogenation at about 800°C. Figure 2. The intensity of hydrogen evolution varied within the mentioned temperature interval and was determined by diffusion rate of hydrogen in the phases towards powder particle surface. The most intensive dehydrogenation with evolution of a major portion of hydrogen from the material was observed within 400-600°C range, due to the formation of the β phase, in which hydrogen diffusivity is fastest. Decrease in hydrogen concentration led to the α phase formation at 600-650°C as a final product of dehydrogenation, and to evolution of a small portion of residual hydrogen from the α phase at further heating up to 800°C.

Figure 1. Crushed TiH₂ particles in green compact. Cracks in the particles are indicated by arrows.

Figure 2. Hydrogen evolution and shrinkage behavior of TiH₂ and Ti compacts upon heating. The temperature intervals of phase fields under dehydrogenation process, determined by in situ X-ray analysis, are indicated at the top.

Significant volume changes upon dehydrogenation resulted in a much more considerable shrinkage of TiH₂ compacts as compared to Ti compacts, Figure 2. Shrinkage of TiH₂ compacts is determined by dehydrogenation (below 800°C) and sintering of powders, and the contribution of the latter becomes apparent at the final stage of dehydrogenation and at higher temperatures. Contrary, the volume changes observed for Ti compacts were determined by powder sintering only.
One more very important feature of TiH₂ heating is the release of H₂O observed within the interval of hydrogen emission. Figure 3. A low-temperature H₂O peak was present for both TiH₂ and Ti compacts and related to the atmospheric moisture absorbed on the powders. However, another H₂O peak was observed for TiH₂ compacts above 400°C, but absent for Ti compact. The emission of H₂O during hydrogen evolution can be explained by the reduction of surface oxide scales and cleaning the powder particle surfaces by atomic hydrogen evolved: TiO₂ + 4H → Ti + 2H₂O. The possibility of this reaction prior to the transition of hydrogen from atomic into molecular state was earlier predicted by theoretical calculations.

The dehydrogenation at heating stage, with inherent phase transformations, volume changes, and reduction of surface oxides, is a distinct feature of TiH₂ application, and has beneficial consequences which affect the sintering and properties of final material.

The phase transformations and significant shrinkage due to decrease in hydrogen concentration results in an increased amount of crystal lattice defects, and, hence, activation of diffusion processes. The high specific surface of TiH₂ particles crushed upon compaction also contributes to an acceleration of diffusion and improved sintering at further heating. Moreover, a cleaning effect of hydrogen evolved has two useful consequences.

The oxide scales at powder surface are effective barriers for diffusion, preventing the sintering of compacted particles. For titanium powder, sintering becomes possible above ~ 700°C when dissolution of TiO₂ scales occurs due to diffusion of oxygen atoms from the surface deep into titanium. For titanium hydride, hydrogen leaving a particle reduces surface oxide scales (at least partially) before their dissolution, thus promoting a mass transfer between particles and decreasing oxygen content in dehydrogenated titanium.

As a positive effect of all these factors, dehydrogenation resulted in the formation of highly activated titanium and its improved sintering as compared to a common Ti powder. It is seen from Figure 2 that above 800°C when dehydrogenation is already completed, the initially hydrogenated compact demonstrated noticeably more active shrinkage than titanium sample. First diffusion contacts between TiH₂ particles formed under heating already at 710°C, i.e., before the dehydrogenation completion.

Calculations of the density changes, based on the corresponding dilatometric curves and density of green compacts, suggest that the density of TiH₂ compacts gets close to that of Ti compacts (3.46 and 3.49 g/cm³) at the final stage of dehydrogenation (800°C). The initially hydrogenated compacts demonstrated a considerable density raise upon following heating, leaving behind the Ti compacts already at 850°C and attaining a higher density (4.15 g/cm³) than the Ti compacts (4.08 g/cm³) when heated to 1250°C. This advantage in density, achieved upon heating, is preserved during further isothermal exposure.

The cleaning effect of hydrogen on the material becomes evident from the measurements of oxygen content in final CP-Ti. The material sintered from TiH₂ powder contained 0.15% O while that obtained from Ti powder-0.20%.

3.2 Influence of Alloying Elements

The alloy synthesis includes the chemical homogenization and corresponding microstructure evolution of powder compacts in addition to pore healing and grain growth which proceed upon CP-Ti sintering. The pore healing and grain growth are interrelated and competitive processes, development of which upon synthesis determines properties of final alloys. The pores are effective stoppers for grain boundary movement, preventing grain growth; on the other hand, a significant grain growth leads to worse healing of pores. As an ideal situation to achieve the high mechanical properties of the synthesized alloys, homogenization and pore healing have to be fully completed before an excessive grain growth will commence. The attainment of a uniform concentration of alloying elements over the titanium matrix was not a problematic matter for all studied compositions. Figure 4, however, fine residual pores (1.5-4% volume fraction) were always present in the final alloys, while average grain size reached 75-180 µm depending on an alloy composition. Table 1. As all processes during the synthesis are controlled by joint diffusion in multicomponent Ti-based systems, the diffusivities of individual alloying elements influence their features.

The elements with high diffusivity rates like Fe and Cr usually favor densification and homogenization of titanium-based compacts, while elements with slow diffusivity like Mo have an opposite effect. However, the cumulative influence of several alloying elements often has an unpredictable effect on densification. The densification behavior and final density of Ti-64 compo-
The $\beta$ stabilizing alloying elements easily saturate the $\beta$ titanium, but hardly penetrate in the $\alpha$ phase due to their extra low solubilities in the HCP lattice. Unlike the $\beta$ stabilizers, Al easily saturates $\alpha$ titanium due to its high solubility there. So, the phase composition of titanium matrix around alloying particles controls the diffusion penetration of alloying elements in titanium, thus affecting homogenization and densification of compacts. Comparatively slow heating ($7^\circ C/min$) of titanium hydride resulted in the formation of $\alpha$ titanium at 600-650$^\circ C$ (see part 3.1) as a final product of the dehydrogenation process. The $\alpha$ state of titanium matrix is favorable for Al diffusion from alloying particles already at relatively low temperatures, resulting in a saturation of titanium with aluminum and thus, stabilization of $\alpha$ areas during heating up to 1000$^\circ C$ and higher. The $\alpha$ areas around alloying particles act like barriers for a redistribution of the $\beta$ stabilizers which are “trapped” in alloying particles. For this reason, the positive potential of fast diffusing Fe and Cr was not realized during heating to high temperatures. An active redistribution of the $\beta$ stabilizers over the titanium matrix starts just after a temperature increase leads to the $\alpha \rightarrow \beta$ transformation even in the areas enriched with Al. This suggests that the peculiarities of synthesis are determined not only by the diffusion rates of alloying elements included, but also by a phase composition of titanium matrix. A retarded redistribution of $\beta$ stabilizers and its subsequent acceleration at high temperatures were observed for all studied compositions, affecting their densification and microstructure evolution. This effect was especially negative for Ti-1023 due to the presence of iron which fast diffusivity was inactive in the beginning and then abruptly became activated at higher temperatures, promoting intensive grain growth. Grain growth prevented a sufficient healing of pores in Ti-1023 alloy and resulted in a reduced final density of 96%. The negative influence of delayed homogenization on the competition of grain growth and densification was less pronounced for Ti-5553 and especially, Ti-64 compositions, Figure 5, Table 1 (items 1-4), because the lower diffusivities of Cr, V and Mo in titanium did not result in a fast grain growth at high temperatures.

To heighten density without an excessive grain coarsening, the potential of fast diffusing alloying elements should be realized at relatively low temperatures before a considerable grain growth occurred.

The application of titanium hydride instead of conventional titanium as starting material creates a unique possibility to control the phase composition of titanium matrix upon dehydrogenation, based on the fact that the hydrogen is an effective $\beta$ stabilizer for titanium. Since an increase in the heating rate extends dehydrogenation to higher temperatures, the application of suf-

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**Figure 4.** Typical microstructure of BEPM produced alloy (Ti-5553 composition)

**Table 1.** Properties of titanium alloys produced by sintering at 1250$^\circ C$ using TiH$_2$ base powder

<table>
<thead>
<tr>
<th>#</th>
<th>Alloy</th>
<th>Rel. density %</th>
<th>Grain size, µm</th>
<th>YS, MPa</th>
<th>UTS, MPa</th>
<th>EL, %</th>
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<tbody>
<tr>
<td>1</td>
<td>CP-Ti</td>
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<td>180</td>
<td>490</td>
<td>562</td>
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<td>2</td>
<td>Ti-6Al-4V</td>
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<td>885</td>
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<tr>
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<td>8</td>
</tr>
<tr>
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</tbody>
</table>

* fast heating rate, sintering at 1200$^\circ C$

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**Figure 5.** Influence of total composition of TiH$_2$ based powder compacts on their shrinkage behavior upon heating. Curve for Ti-6Al-4V compact (not shown) is very similar to that for Ti-10V compact
ficiently high heating rate results in stabilizing the $\beta$ phase with hydrogen and prevents the $\alpha$ phase formation during heating up to $882^\circ$C. Under the conditions of a fast heating, the great potential of Fe fast diffusion in the $\beta$ titanium realizes at relatively low temperatures due to the absence of $\alpha$ phase barriers. Upon the fast heating to $1000^\circ$C, the sequence of the alloying element penetration in the titanium matrix changed and an intense Fe diffusion in titanium was observed simultaneously with aluminum penetration. Figure 6. These changes in the alloying element redistributions led to an improved densification even at the decrease in sintering temperature from $1250^\circ$C down to $1200^\circ$C, providing formation of Ti-1023 alloy with a higher density (98%) and a lower average grain size, Table 1, item 5. This combination of fine grains and improved density promotes attainment of high mechanical properties even in a strengthened condition.

![Figure 6. Redistribution of alloying elements in the Ti-10V-2Fe-3Al compact after fast heating to 1000°C.](image)

The optimization of dehydrogenation and sintering parameters depending on alloy compositions allows the attainment of a high balance of mechanical properties, sufficient for practice applications of BEPM materials. All synthesized compositions demonstrated high tensile properties comparable with the properties of corresponding cast/wrought alloys.

4. Conclusions

(1) The positive role of hydrogen at compaction stage becomes apparent in a specific fine-porous microstructure of compacted TiH$_2$ powder, which favors pore healing upon further sintering.

(2) Cleaning of surface scales, phase transformations and volume changes observed upon the heating stage due to hydrogen evolution from titanium provide activation of diffusion, improved densification and decrease in oxygen content in the final materials.

(3) The diffusion mobilities of alloying elements in titanium and a phase composition of titanium matrix determine the chemical homogenization process. The presence of a stabilizer Al together with the fast diffusing $\beta$ stabilizer Fe can negatively affect homogenization and densification.

(4) Application of hydrogenated titanium as a starting material gives an opportunity to control the $\alpha/\beta$ phase composition of the titanium matrix upon dehydrogenation and, in this way, to regulate the sequence of alloying element penetration in titanium, positively affecting microstructure and density of synthesized alloys.

REFERENCES