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Revealing dehydrogenation effect and resultant densification mechanism during pressureless sintering of TiH₂ powder



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ABSTRACT

The use of TiH₂ powder as a sintering precursor can produce nearly full-density titanium and titanium alloys with good mechanical properties. Unfortunately, there is a lack of research on the effect of lattice defects generated during the dehydrogenation of TiH₂ powder, and the underlying sintering diffusion mechanism and activation energy have yet to be determined. In this work, we report a two-step sintering strategy to reveal the dehydrogenation effect and resultant densification mechanism during the pressureless sintering of a TiH₂ powder precursor. The results show that, compared with hydrogenated-dehydrogenated (HDH) Ti powder, TiH₂ powder, an intermediate of HDH-Ti powder, exhibited a higher instantaneous densification rate, greater onset relative density, rapid grain growth, and thus a smaller grain size. It also showed a grain boundary diffusion mechanism below 91% relative density and half the sintering activation energy in the intermediate sintering stage. Fundamentally, this was attributed to lattice defects generated during the dehydrogenation of TiH₂ powder, which was confirmed by the greater relative density of a sintered TiH₂ compact due to the twostep sintering strategy designed herein. Interestingly, the sintered sample obtained from the TiH₂ powder precursor has a satisfying combination of strength and ductility that is far superior to other bulk Ti materials, especially sintered bulk Ti obtained from HDH-Ti powder. The results obtained in this paper provide theoretical guidance for using pressureless sintering to produce nearly full-density Ti and Ti alloys with good mechanical properties for structural applications.

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1. Introduction

Due to their low density, high specific strength, good ductility, and excellent corrosion resistance [1,2], titanium and its alloys are wildly used as structural materials in the aerospace, automotive, military, and chemical industries. As an extremely important material forming approach, powder sintering allows the low-cost production of Ti components while reducing material waste [3–6]. Generally, it is difficult to achieve nearly full-density Ti components via the pressureless sintering of Ti powder, and they are commonly produced by the hydrogenation-dehydrogenation (HDH) method. The reason, the densification of HDH-Ti powder is insufficient to eliminate the majority of pores before rapid grain growth, which gives rise to pore-boundary separation, in which residual pores

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https://doi.org/10.1016/j.jallcom.2021.159792 0925-8388/© 2021 Elsevier B.V. All rights reserved. separate from grain boundaries, remain in the grain interior, and finally entrapped in the sintered products [7]. The relative density of pressureless-sintered components obtained using HDH-Ti powder is typically lower than 98% [8,9].

In addition to pressure-assisted sintering methods such as spark plasma sintering [10–14], hot isostatic pressing [15,16], vacuum hot pressing [17,18], novel additive manufacturing [19–21] and sever plastic deformation methods [22], an effective strategy for obtaining nearly full-density bulk Ti and Ti alloys is to use TiH₂ powder instead of HDH-Ti powder as the starting material. This strategy has three well-known advantages. First, HDH-Ti powder is produced by hydrogenating Ti raw material, milling titanium hydride into a powder, and finally dehydrogenating milled titanium hydride powder; therefore, TiH₂ powder is an intermediate of HDH production and is cheaper than HDH-Ti powder. Second, the hydrogen in TiH₂ powder can be employed as a temporary alloying element to control phase transformation and induce grain refinement, which can improve the mechanical properties [5,23,24]. For example, an ultrafine lamellar Ti–6Al–4V alloy with an ultimate strength of 1431 MPa and 4.5% elongation was obtained by the hot-extrusion of TiH₂/60Al40V blended powder [23]. Third and most importantly, compared with HDH-Ti powder, the use of TiH₂ powder as the starting sintering material induces faster densification and produces sintered Ti components with a higher relative density. Specifically, the relative density can reach as high as 98.5–99.5% by pressureless vacuum sintering [25,26] or hydrogen sintering and phase transformation [27–29], which is equivalent to the corresponding pressure-assisted sintering methods.

Powder shrinkage and densification are macroscopic manifestations of pore elimination and atomic diffusion under the influence of various factors, including the intrinsic properties of powders [7], pressing and sintering parameters [30], defect concentration [31], impurities [32,33], etc. In essence, densification mechanisms are associated with specific physical quantities including the densification rate (ϕ) , time exponent (n), activation energy (O), comprehensive impact factor, etc. [31,34,35]. To date, some efforts have been made to investigate the sintering behavior of TiH₂ and HDH-Ti powders, yet only the differences in shrinkage and final relative density were compared [32,36]. Notably, no research has quantitatively compared the sintering densification mechanism of the two types of powders from the perspective of the diffusion mechanism and sintering activation energy, which are significant issues for powder sintering. Two main effects account for the greater densification of TiH₂ powder. The first is the elimination of atomic diffusion by producing a hydrogen-thinned oxide layer due to evolved hydrogen. The second is the acceleration of densification due to extra defects generated by phase transformation during dehydrogenation [37]. Revealing the related sintering mechanism and illustrating the limitations of these two effects are crucial for achieving nearly fulldensity bulk materials. Some investigations have verified a reduction in the oxygen content by water generation during the dehydrogenation of TiH₂ powder [36,38–41] and, thus, the promotion of sintering densification [25,42]. Unfortunately, no work has clarified the existence and impact of the aforementioned defects generation, which might plays a critical role in the sintering of TiH₂ powder.

The purpose of this work was to reveal the dehydrogenation effect and resultant densification mechanism during the pressureless sintering of TiH₂ powder to supplement the sintering mechanism of TiH₂ powder and help select appropriate sintering parameters to fabricate nearly full-density Ti components with good mechanical properties. To that effect, TiH₂ and HDH-Ti compacts were sintered through isothermal and non-isothermal methods, and their shrinkage during sintering and mechanical properties were quantitatively compared. In particular, grain growth, diffusion mechanism, and activation energy were determined, and the effects of dehydrogenation on densification and their limitations were discussed in detail.

2. Materials and experimental methods

The as-received powders were – 325 mesh TiH₂ (O: 0.24 wt%) and HDH-Ti (O: 0.19 wt%) powders supplied by CW Nano Technology Co., Ltd., China, whose morphologies are shown in Fig. 1. The two powders have irregular shapes with the same particle size; therefore, the powder shape and size should have a negligible influence on the sintering densification in this work. The two types of powders were uniaxially pressed at a pressure of 600 MPa and held for 30 s to produce green compacts by a hydraulic machine. Subsequently, all green compacts were subjected to pressureless sintering. A dilatometer (NETZSCH DIL 402 PC) was applied to collect shrinkage data of TiH₂ and HDH-Ti compacts with dimensions of 5 mm × 5 mm× 20 mm. All compacts heated in the dilatometer were protected by a high-purity (99.999%) Ar atmosphere. Non-isothermal sintering was conducted to investigate powder shrinkage and further

determine the sintering activation energy. The related sintering parameters were selected to be: heating to 1250 °C and holding for 4h at various heating rates of 2°C/min, 5°C/min, 10°C/min, and 15 °C/min, respectively. Isothermal sintering was used to estimate the diffusion mechanism, by heating to 950 °C, 1000 °C, 1050 °C, 1100 °C, and 1150 °C at 15 °C/min, with a dwell time of 2 h. To examine the grain size evolution under different sintering temperatures and holding times, the two types of green compacts with dimensions of 62.5 mm × 13.5 mm × 15 mm were heated to 1050 °C, 1100 °C, and 1150 °C at 10 °C/min without holding, or to 1250 °C at 10 °C/min and holding for 0, 1, 2, and 4 h, respectively. This was followed by rapid cooling to ambient temperature in a flowing highpurity Ar atmosphere. The grain size was measured optically and determined using ImageJ software. A two-step sintering strategy was designed and employed to illustrate the dehydrogenation effects. Specifically, the dehydrogenation behavior of a ϕ 3 mm×2 mm TiH₂ green compact was studied under a high-purity Ar atmosphere in a NETZSCH STA 449F3 DSC by heating to 870°C at 10°C/min, cooling to ambient temperature, then heating to 1250 °C at 10 °C/ min, and holding for 4 h. All samples for microstructure observations were polished by abrasive paper, etched by Kroll solution (2 mL HF: 4 mL HNO₃: 100 mL H₂O), and finally characterized by scanning electron microscopy (SEM, FEI Nova Nano SEM 430) and optical microscopy. To evaluate the mechanical properties, 62.5 mm × 13.5 mm× 15 mm green compacts were sintered at 1100 °C and 1250 °C at 10 °C/min with a dwell time of 4 h under Ar protection. The tensile samples with a gauge size of 16 mm, width of 2.5 mm, and thickness of 2 mm, were machined according to ASTM E9-81 from as-sintered bulk Ti and then tested using a universal testing machine under quasi-static loading at a strain rate of 5×10^{-4} s⁻¹. The oxygen contents were measured by a TC600 Nitrogen/Oxygen analyzer (LECO Co., USA). The density of the as-sintered specimens was analyzed by Archimedes' method.

3. Results

3.1. Shrinkage behavior

Fig. 2a presents the shrinkage-temperature curves of the TiH₂ and HDH-Ti green compacts at different heating rates. It is found that the HDH-Ti compacts began to shrink near 878 °C with a total linear shrinkage of about 3.5% until 1250 °C. In contrast, the TiH₂ compacts had a far lower initial shrinkage temperature around 320 °C and, thus, a far greater linear shrinkage of about 11%. The DSC curve of the TiH₂ compact (Fig. 2a inset) measured at 10 °C/min shows a remarkable endothermic peak starting at 332 °C and ending at 861 °C (lower than the phase transition temperature of HCP Ti \rightarrow BCC Ti). The corresponding TG curve presents a 3.09% total weight loss in the same temperature range. These two events indicate that the TiH₂ compacts were dehydrogenated from 332 °C to 861 °C. Since the phase transformation from FCC TiH₂ to HCP Ti is accompanied by volumetric shrinkage and weight loss induced by dehydrogenation, the shrinkage of the TiH₂ compacts before approximately 861 °C was attributed to dehydrogenation. The exact dehydrogenation ending temperatures of the TiH₂ compacts were obtained by analyzing the shrinkage curves with various heating rates of 2 °C/min, 5 °C/min, 10 °C/min, and 15 °C/min, and are 856 °C, 859 °C, 873 °C, and 892 °C, respectively. To directly compare the sintering densification behaviors of the Ti and Ti_H compacts (transformed from the HDH-Ti and TiH₂ green compacts), the shrinkage curves of the TiH₂ compacts were corrected by removing the shrinkage of dehydrogenation effect, as shown in Fig. 2b. Both Ti and Ti_H compacts began to densify near the HCP Ti \rightarrow BCC Ti phase transition temperature due to the enhanced self-diffusivity in the BCC Ti region [28,43]. Furthermore, the shrinkage of both compacts increased upon decreasing the heating rate at a given temperature, possibly because the lower



Fig. 1. SEM images of the as-received TiH₂ (a and c) and HDH-Ti (b and d) powders.

heating rate provides a longer sintering time. Interestingly, the Ti_H compacts have a distinctly higher linear shrinkage rate than the corresponding Ti compacts at a given heating rate at temperatures below approximately 1170 °C (Fig. 2b). Meanwhile, the Ti_H compacts displayed a total linear shrinkage of about 6%, far greater than that (3.5%) of the Ti compacts. Undoubtedly, these results indicate that there is a unique densification mechanism due to dehydrogenation during the pressureless sintering of TiH_2 compacts.

During pressureless sintering, the relative density of the sintered compact $\rho_x(\%)$ at any temperature can be calculated from the linear shrinkage by [44]:

$$\rho_x = \rho_f \left(\frac{1 - \Delta L_f / L_0}{1 - \Delta L_x / L_0} \right)^3 \tag{1}$$

where $\rho_f(\%)$ refers to the final relative density of the sintered compact, L_0 is the initial length of the green compact, ΔL_f is the final length change after sintering, and ΔL_x is the instantaneous length change at any temperature corresponding to the relative density ρ_{ν} .

Table 1 lists the initial and final densities, peak densification rate, and corresponding temperature of the TiH_2 and Ti compacts at various heating rates. The initial density of both compacts after pressing was measured to be about 84% (Fig. 2b). In contrast, the



Fig. 2. (a) Shrinkage-temperature curves of the TiH₂ and HDH-Ti green compacts at different heating rates. a inset shows the TG and DSC curves of the TiH₂ green compact. (b) Corresponding shrinkage curves after removing shrinkage resulting from dehydrogenation.

Table 1

The initial and final density, peak densification rate, and corresponding temperature for the TiH_2 and Ti compacts sintered at various heating rates.

Compact	Heating rate (°C/min)	Initial density (%)	Final density (%)	Peak densification rate (×10 ⁻³ %/s)	Peak densification temperature (°C)
TiH ₂	2	84.3	97.5	2.3	1032
	5	84.6	96.5	5.5	1058
	10	84.5	95.8	10.4	1060
	15	84.2	95.0	14.8	1082
Ti	2	84.3	94.6	1.4	1080
	5	84.6	94.1	3.1	1115
	10	84.7	92.4	6.0	1193
	15	84.2	91.8	10.1	1194

density of the TiH₂ compact after dehydrogenation decreased to 79–81% (Figs. 2 and 3a), decreasing upon increasing the heating rate (Fig. 3a) due to the almost constant pore volume and the decreased volume of the TiH₂ sintered entity during dehydrogenation. A similar phenomenon was also observed in the sintering of a TiH₂ compact [45]. Fig. 3b shows the instantaneous densification rate $(d\rho/dt)$ vs temperature curves of the Ti_H and Ti compacts at various heating rates. Evidently, the instantaneous densification rate increased upon increasing the heating rate at a given temperature for each sintered compact (Fig. 3b). Meanwhile, the TiH₂ compacts displayed a far greater peak densification rate and lower peak densification temperature than the corresponding Ti compacts at a given heating rate (Table 1). Taking 10 °C/min as an example, the Ti_H compact reached a peak densification rate of 10.4×10^{-3} % at 1060 °C, while the corresponding Ti compact was 6.0×10^{-3} % at 1193 °C. The higher peak densification rate and lower peak densification temperature make it possible to produce nearly full-density bulk materials via low-temperature sintering of the TiH₂ compacts. Generally, powder compacts pressed with a lower initial relative density usually densify faster during sintering, but they achieve lower final densities after sintering [7]. On the contrary, in this work, although the Ti_{H} compacts after dehydrogenation obtained a lower relative density (79.3%) than the Ti compact (84.7%) at 10 °C/min, it reached a higher relative density of 95.8% than the Ti compact (92.4%) after sintering at 1250 °C (Fig. 3a). It can be concluded that there are significant causes accounting for the higher peak densification rate and lower peak densification temperature and higher final relative density of the Ti_H compacts.



Fig. 4. Tensile stress-strain curves of Ti_H and Ti samples sintered by heating to 1100 °C and 1250 °C at 10 °C/min and dwelling for 4 h. The insets show the corresponding optical microstructures of the two types of bulk samples.

3.2. Mechanical properties

Fig. 4 displays the tensile stress-strain curves of the Ti_H and Ti samples sintered by heating to 1100 °C and 1250 °C at 10 °C/min and dwelling for 4h. The corresponding tensile mechanical property values are listed in Table 2. The relative density of the Ti_H samples exceeded 98%, a threshold density that ensures ductility, while the relative density of the Ti samples was lower than this. Sample Ti_H-1100, when sintered at a far lower temperature (1250 °C) than typically used in sintering [25], has a density as high as 98.5%, compared to only 96.2% of the sample Ti-1100. This high densification of Ti_H-1100 was attributed to enhanced atomic diffusion in the TiH₂ compact sintered at 1100 °C, coinciding with its peak densification temperature of 1060 $^{\circ}$ C (Fig. 3b and Table 1). The Ti_H samples have a satisfying combination of yield strength, ultimate strength, and elongation, which are respectively 93 MPa, 133 MPa, and 3.3% higher than the corresponding values of their Ti counterpart. The sintering temperature also significantly affected the relative density and mechanical properties of the Ti samples sintered from HDH-Ti powder. Sample Ti-1250 had a relatively high density of 97.2% as well as a large elongation of 17.8%, vet the corresponding values were 96.2% and 8.25% for sample Ti-1100. This means that 1100 °C is an



Fig. 3. Relative density (a) and instantaneous densification rate (b) vs temperature curves of the Ti_H and Ti compacts at various heating rates.

Table 2

Relative density and tensile mechanical properties of the two types of bulk samples fabricated in Fig. 4. VS: Vacuum sintering; SPS: Spark plasma sintering; VHP: Vacuum hot pressing; SLM: Selective laser melting; Ti-4: Wrought Ti grade 4.

Samples	Yield strength (MPa)	Ultimate strength (MPa)	Elongation (%)	Relative density (%)	Oxygen content (wt%)
Ti _H -1250	533	635	21.1	99.0	0.28
Ti _H -1100	529	659	20.8	98.5	0.27
Ti-1250	409	502	17.8	97.2	0.32
Ti-1100	436	516	8.5	96.2	0.30
Ti-VS [46]	458	549	6.4	97.5	0.37
Ti-VS [47]	407	515	18.4	94.5	0.23
Ti-SPS [14]	595	720	18	99.0	0.31
Ti-SPS [13]	286	364	39.4	>99.0	~
Ti-VHP [18]	404	659	4.84	99.54	0.36
Ti-SLM [21]	533	714	17.8	99.5	0.18
Ti-SLM [20]	502	600	34.3	99.6	0.11
Ti-Forging [48]	490	619	29	100	0.19
Wrought Ti-4 [14]	483	550	15	100	~

inappropriate sintering temperature for HDH-Ti powder. In addition to the higher relative density (Table 2) and the finer grain size (Fig. 4 inset) of the Ti_H samples, the higher oxygen content in a certain range also improves the yield strength. It is interesting to find that the Ti_H samples circumvented the strength-ductility trade-off, and their excellent combination of strength and ductility are far superior to bulk Ti materials produced by vacuum sintering [46,47], and are equivalent to those obtained by pressure-assisted sintering (SPS and VHP) [13,14,18], forging [48], and selective laser melting [20,21], as shown in Table 2. Therefore, applying TiH₂ powder as a starting material is an effective approach for fabricating nearly full-density bulk Ti and Ti alloys, even via pressureless sintering in our case. Additionally, considering the accelerated densification behavior and reduced peak densification temperature of the TiH₂ compacts, it is possible to sinter Ti bulk materials at 1100 °C or even lower. If the homogenization of alloying elements is taken into consideration, this approach can also be used to optimize pressureless sintering parameters of Ti alloys, such as Ti-6Al-4V.

4. Discussion

The results described above clearly demonstrate that sintered TiH_2 powder displays a higher densification rate, greater final relative density, and higher mechanical properties than those of sintered HDH-Ti powder. To quantitatively compare the shrinkage behavior of the two types of powders, the diffusion mechanism and sintering activation energy associated with densification were determined, and the effects of dehydrogenation on the densification mechanism were discussed as follows.

4.1. Diffusion mechanism

Powder shrinkage and densification during powder sintering are usually divided into three overlapping stages according to the relative density [49], i.e., the initial (<66%), intermediate (66–92%), and final stages (>92%). The relative density change in the initial stage was limited to 2–3% [7], and the most evident shrinkage and densification occurred during the intermediate stage. The maximum densification difference between the Ti_H and Ti samples in this work arose during the intermediate stage (Fig. 3). As for the mass transport responsible for the sintering densification mechanism in this stage, there are two diffusion mechanisms to consider: lattice diffusion and grain boundary diffusion.

In general, linear shrinkage during powder sintering follows a power-law relationship versus the isothermal holding time t. The relationship can be used to fit a large part of the sintering process, including the initial and intermediate stages, when grain growth is limited [50]. The corresponding equation can be expressed as [31,51]:

$$\frac{\Delta L}{L_0} = \left(\frac{H(T)}{G^m}\right)^n t^n \tag{2}$$

where H(T) represents a function based on temperature and is related to geometry and property parameters of power particles: $G(\mu m)$ is the grain size, m and n are exponents associated with the diffusion mechanism, and t (s) is the isothermal holding time. For each dominant diffusion mechanism during solid sintering, Eq. (2) varies primarily in the time exponent n, grain size exponent m, and form ofH(T). Taking the logarithm of both sides, Eq. (2) can be written as:

$$\ln\left(\frac{\Delta L}{L_0}\right) = n \ln t + n \ln\left(\frac{H(T)}{G^m}\right)$$
(3)

During an isothermal hold, H(T) can be regarded as constant. Assuming negligible grain growth (increase < 20%), n can be obtained by fitting the slope of the function $\ln(\Delta L/L_0)$ versus lnt. Specifically, diffusion mechanisms can be classified as either grain boundary diffusion or lattice diffusion when n = 0.25-0.35 or n = 0.4-0.5 [35,51-53], respectively. Hence, the dominant diffusion mechanism was determined herein by isothermal sintering at various temperatures inside the intermediate sintering stage.

Fig. 5 presents the relationship between the grain size and relative density of the Ti_H and Ti samples, which were obtained by measuring the two types of bulk samples prepared by heating the



Fig. 5. The relationship between the grain size and relative density of the Ti_H and Ti samples after heating green compacts to 1050, 1100, 1150, and 1250 °C and holding for 0, 1, 2, and 4 h at 10 °C/min. The insets illustrate the microstructure evolution of the Ti_H samples with relative densities of 86.8% and 92.4%.

Table 3

Relative density and corresponding grain size of Ti_H and Ti compacts heated to 1050, 1100, 1150, and 1250 °C and held for 0, 1, 2, and 4 h at 10 °C/min, respectively.

Sample	Sintering parameter	1050 °C for 0 h	1100 °C for 0 h	1150 °C for 0 h	1250 °C for 0 h	1250 °C for 1 h	1250 °C for 2 h	1250 °C for 4 h
Ti _H	ρ (%)	86.8	89.9	92.4	95.8	98.5	98.8	99.2
	G (µm)	29.2	31.4	35.4	47.6	87.0	93.6	189.1
Ti	ρ(%)	86.9	88.0	89.6	93.0	96.7	97.0	97.4
	G (µm)	28.1	29.2	34.4	39.6	96.5	106.6	239.2

two types of green compacts to various temperatures of 1050, 1100, 1150, and 1250 °C and holding for 0, 1, 2, and 4 h at 10 °C/min. The obtained values are listed in Table 3. As an example, the insets show that the grain size increased and the pore volume decreased as the relative density increased. In other words, the grain sizes of 29.2 µm and 35.4 µm correspond to relative densities of 86.8% and 92.4% for the Ti_H samples. Furthermore, the grain size increased quickly to 189 µm at 99.2% relative density. Similarly, the grain growth in the Ti samples followed the same trend. Sample Ti_H has a 60 µm smaller grain size than that of the Ti sample fabricated under the same sintering parameters, i.e., heating to 1250 °C and holding for 4 h at 10 °C/min. The pores, especially those located along grain boundaries, reduced the contact area of adjacent grains and, thus, impeded atom diffusion and exchange across grain boundaries, thereby slowing grain growth in the sintered compacts. As a result, grain growth is usually restrained in the low relative density stage, specifically in the intermediate stage of powder sintering [54]. Based on this notion, the onset of grain growth was delayed at a relative density of approximately 90%. Also, the experimental results in Fig. 5 demonstrate that grain size in both samples remained almost unchanged until the relative density exceeded 91%. Rapid grain growth in the Ti_H samples occurred when the relative density exceeded 96%, 3% higher than the Ti samples. This indicates a finer grain size (189 μ m) in the nearly full-density Ti_H sample compared with that $(239 \,\mu\text{m})$ in the Ti sample (Table 3 and Fig. 5), which supports the idea that applying the TiH₂ powder as a starting material produces bulk Ti and Ti alloys with finer-grained structures and better mechanical properties.

Fig. 6 displays the relationship between the logarithm of the sintering time and relative shrinkage for the Ti_H and Ti samples. Since grain growth is negligible at a relative density below 91% (Fig. 5), the relative shrinkage data were selected from 2 h isothermal sintering curves when heated to 950, 1000, 1050, 1100, and 1150 °C at 15 °C/min. The values did not exceed the critical value of 91% and were fitted according to Eq. (3). As such, the *n* values

associated with the diffusion mechanisms were calculated and decreased from 0.33 at 950 °C to 0.25 at 1050 °C and then further decreased to 0.13 at 1150 $^\circ$ C for the Ti_H samples, and from 0.34 at 950 $^\circ$ C to 0.27 at 1100 °C and then further to 0.16 at 1150 °C for the Ti samples (Fig. 6), respectively. When n = 0.33 - 0.25, corresponding to grain boundary diffusion [35,51], it can be deduced that powder densification at a relative density below 91% is controlled by grain boundary diffusion in the Ti_H samples from 950 to 1050 °C and in the Ti samples from 950 to 1100 °C, respectively. Herein is the first report of a specific sintering densification mechanism for Ti_H compacts obtained from TiH₂ powder. The deduced grain boundary diffusion mechanism in this paper is similar to that when sintering 45 µm Ti-6Al-4V powder up to 1100 °C and 90% relative density [34], sintering 20µm titanium powder up to 1150 °C [55], sintering 40µm copper powder [56] and 15 µm stainless steel powder below 90% relative density [57], et al. In addition, the grain boundary diffusion in the Ti_H samples occurs at a lower sintering temperature than the Ti samples, making it possible to achieve nearly full-density at a lower sintering temperature.

4.2. Sintering activation energy

Powder shrinkage densification in the intermediate sintering stage can be theoretically expressed as [7]:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = 854 \frac{D_b \delta_b \gamma V_m}{RG^4 T} \left(\frac{1}{P_v}\right)^{0.5} \tag{4}$$

where D_b (m²/s) is the grain boundary diffusion coefficient, δ_b (nm) is the diffusion distance of the grain boundary, which is equal to the grain boundary thickness, γ is the surface energy (J/m²), V_m (m³/mol) is the molar volume of sintered compacts, *R* (8.314 J/K mol) is the gas constant, *T* (K) is the absolute temperature, and P_v is the volume fraction of pores.



Fig. 6. The relationship between the logarithm of the sintering time and relative shrinkage for the Ti_H (a) and Ti (b) samples by isothermal sintering for 2 h at 950, 1000, 1050, 1100, and 1150 °C (heating rate: 15 °C/min).



Fig. 7. Plots of $\ln(TP^{0.5}(d\rho/dt))$ vs. 1/T of the TiH₂ and HDH-Ti compacts at various heating rates. The inset lists the sintering activation energies of grain boundary diffusion for the Ti_H and Ti samples.

Simultaneously, the grain boundary diffusion coefficient D_b is dependent on the temperature and follows an Arrhenius relationship [58]:

$$D_b = D_0 \exp\left(\frac{-Q}{RT}\right) \tag{5}$$

where $D_0(m^2/s)$ is the pre-exponential factor related to the frequency of atomic jumps, and Q(kJ/mol) is the activation energy for grain boundary diffusion. Subsequently, applying and rearranging Eqs. (4) and (5) and taking the logarithm of both sides, the powder shrinkage behavior can be written as:

$$\ln\left(TP^{0.5}\frac{\mathrm{d}\rho}{\mathrm{d}t}\right) = \ln\left(854\frac{D_0\delta_b\gamma V_m}{RG^4}\right) - \frac{Q}{RT} \tag{6}$$

When grain growth is negligible, $\ln(854 \frac{D_0 \delta_b \gamma V_m}{RG^4})$ can be regarded as a constant, and the activation energy *Q* is determined as the slope of the linear fit of $\ln(TP^{0.5}(d\rho/dt))$ versus 1/*T*. The selected data used for linear fitting abide by two rules: located inside the intermediate sintering stage and belonging to grain boundary diffusion. Finally,

the determined values of Q are shown in Fig. 7. Q for the Ti samples are 142.4, 138.2, and 133.5 kJ/mol at heating rates of 2, 5, and 10 °C/ min, respectively. These results accord with those (113–158 kJ/mol) reported for β-Ti grain boundary diffusion [55,59]. Surprisingly, the Q values for the Ti_H samples are lower than the corresponding values of the Ti samples, which are 71.3, 67.6, 62.7, and 56.4 kJ/mol at different heating rates, respectively. This indicates that the Ti samples have a slower atomic diffusion rate than the Ti_H samples in the intermediate sintering stage before rapid grain growth. For instance, at a heating rate of 10 °C/min, the grain boundary diffusion coefficient of Ti_{H} and Ti samples were calculated using Eq. (5) as and $D_{\text{Ti}} = D_0 \exp(-133.5/RT)$. It has been reported that if sufficient densification is achieved before pore-boundary separation, sintered compacts can have a relatively high final density and relatively fine grains [7,49]. This is confirmed in Fig. 5, in which the Ti_H samples reached 96% density before pore-boundary separation, thereby producing a higher density (99.2%) and finer grain (189 µm) compared with the Ti samples. In addition, the lower Q of the Ti_H samples explains why the TiH₂ powder can also be sintered at a lower temperature (1100 °C or even lower) while still fabricating nearly full-density bulk materials (>98%) with comparable tensile properties (Fig. 4).

4.3. Effect of dehydrogenation on the densification mechanism

Herein, the physical properties affecting powder shrinkage and densification, such as the morphology and average particle size of initial TiH₂ and Ti powders (Fig. 1), and the fabrication parameters, including the heating rate, were held constant. The only phase in both Ti and Ti_H samples in the intermediate sintering stage (T > $\alpha \leftrightarrow \beta$ transition temperature) was BCC β -Ti; therefore, the accelerated densification behavior of the Ti_H samples at the intermediate sintering stage was mainly attributed to dehydrogenation of the TiH₂ precursor from 320 to 860 °C ($T < \alpha \leftrightarrow \beta$ transition temperature).

TiH₂ has an FCC lattice structure with H atoms located in tetrahedral voids and H atoms that can be easily released from the Ti lattice at elevated temperatures in a vacuum. There are two main effects accounting for the accelerated densification of the TiH₂ precursor depending on the dehydrogenation mechanism (Fig. 8). One is a self-purification effect through water (H₂O) generation in which released H reacts with O on the surface of TiH₂ powder, which reduces



Fig. 8. Schematic diagram of the two types of dehydrogenation effects in the TiH₂ compact: (I) self-purification and (II) defects generation.

the oxide layer thickness [25,42]. Since O can act as an obstacle to atomic diffusion, Ti powder with a purified surface is beneficial for powder shrinkage and densification [33,60]. Another is defects generation, in which extra vacancies and dislocations are introduced by large volumetric changes due to dehydrogenation during the transformation from FCC-TiH₂ to HCP-Ti. Therefore, the surface energy increases, and atomic diffusion accelerates [36,37,45]. To date, the self-purification effect has been theoretically supported by ΔG for the reaction between H atoms and oxides (Ti₂O₃, TiO₂, and TiO) [38], and experimentally by the water generation and weight loss during dehydrogenation [32] and the oxygen content decrease of 0.05 wt% after sintering a TiH₂ compact [42]. However, few investigations have testified the defects generation on dehydrogenation, which is crucial for fabricating nearly full-density Ti bulk materials.

The FCC-TiH₂ to HCP-Ti phase transformation is multi-step process, in which the TiH₂ (a = 0.444 nm) phase transforms into metastable FCT-TiH (a = 0.420 nm, c = 0.470 nm) and finally to HCP-Ti (a = 0.295 nm, c = 0.295 nm)c = 0.468 nm) [61]. Fig. 8 illustrates the starting and ending states of the lattice. The total volume change by determining the volume per atom (V) is calculated as below. The volume per atom (V) was obtained by dividing the volume of a single lattice cell by the nominal number of atoms in the corresponding lattice (4 atoms for an FCC lattice and 6 for HCP). The calculated values of FCC-TiH₂ (V_a) and HCP-Ti (V_b) are 2.19×10^{-29} m³ and 1.76×10^{-29} m³, respectively. Therefore, the volume change for the FCC \leftrightarrow HCP transition calculated using the for $mula(V_a - V_b)/V_a$ was 19.6% (Fig. 8). In addition, the total volume change from FCC to HCP calculated by the deformation gradient tensors of the lattice [61] was 19.4%, which is consistent with the above results. The details of the calculations are shown in Appendix A. Considering the porosity and hypothesizing that the defect concentration remained unchanged during dehydrogenation, the macroscopic volume shrinkage after dehydrogenation of the TiH₂ compact was calculated by $\rho_0 \times 19.6\%$ and was about 16.5%. Nevertheless, the shrinkage for the TiH₂ compacts measured by dilatometry (Fig. 2) was 14.2%, 13.9%, 13.6%, and 13.5% at various heating rates of 2, 5, 10, and 15 °C/min, respectively. The shrinkage difference of 2.3 - 3% might be attributed to an increase in the number of vacancies or dislocation concentration during dehydrogenation.

Fig. 9 shows the DSC curves of TiH₂ powder heated to 870 °C, subsequently cooled to room temperature, and reheated to 870 °C. The endothermic area during heating was calculated to be 98.5 kJ/mol (Fig. 9a), which is ascribed to the phase transformation from FCC-TiH₂ to HCP-Ti induced by the dehydrogenation of the TiH₂ powder. It can be seen that an exothermic event with multiple peaks began at 791 °C and



ended at 387 °C, exhibiting an area of 580.2 I/mol during cooling (Fig. 9b). It is well established that lattice defects raise the Gibbs free energy of metallic materials, and stored energy accumulated by lattice defects can be released via exothermic events at the corresponding recovery temperature $(0.1-0.5 T_m)$ by the relaxation and recovery of defects [31]. This is corroborated by the fact that milling resulted in an exothermic enthalpy of 0.82 ± 0.15 kJ/mol and 0.50 kJ/mol for Fe [62] and Ti [31] powders, respectively. Since the exothermic enthalpy of 580.2 J/mol (Fig. 9b) is almost equivalent to the values due to lattice defects in milled Fe and Ti powders, the exothermic peaks in DSC curves (Fig. 9b) likely correspond to the release of stored energy from lattice defects. The initial stored defects, such as disorder, dislocations, and vacancies from the powder preparation and pressing, recovered during the first heating stage, and dropped to a relatively low concentration. Hence, the recovered defects during the cooling stage almost certainly resulted from dehydrogenation via the FCC-TiH₂ \rightarrow HCP-Ti transformation. This is consistent with the aforementioned conclusion reached by analyzing the lattice volume strain (Fig. 8) and macroscopic shrinkage (Fig. 2).

Furthermore, a two-step sintering experiment was designed and applied to investigate the contribution and limitation of defects generation effects on powder densification. In step I, the TiH₂ compact was heated to 870 °C, which is exactly between the end temperature of dehydrogenation and the onset temperature of powder densification. It was then cooled to room temperature under a high vacuum. In this case, the released hydrogen reacted with the oxide layer, which purified the powder surface (Fig. 8) because O contamination from the surroundings was negligible due to high-vacuum sintering; thus, a self-purification effect appeared, which promoted powder densification during step I. Regarding the defects generation effect, the extra defects introduced from dehydrogenation recovered to a normal concentration when cooling from 870 °C to room temperature, as shown in Fig. 9, which means that the defects generation effect was eliminated during the sintering in step I.

In step II, the sample obtained in step I was re-heated to a sintering temperature of 1250 °C, which produced a densified sintered compact (named TS-Ti). The TS-Ti sample obtained by two-step sintering displayed only a self-purification effect, which accelerated powder densification compared with the Ti_H compacts; thus, it is possible to determine the contribution of the defects generation effects on powder densification by comparing the density of the TS-Ti and Ti_H samples. Specifically, if the density of the TS-Ti sample is lower than that of the Ti_H sample and higher than that of the Ti sample, defects generation significantly contributed to powder densification.

Based on the designed two-step sintering experiment, the TiH₂ compact was heated to 870 °C at 10 °C/min, subsequently cooled to 50 °C in a sintering furnace under 10^{-4} Pa vacuum, and then reheated to 1250 °C at 10 °C/min, with a dwell time of 4 h. The resulting sample was called TS-Ti. For comparison, the TiH₂ and HDH-Ti compacts were heated to 1250 °C at 10 °C/min with a dwell time of 4 h under 10^{-4} Pa vacuum, which were respectively named Ti_H and Ti (consistent with the contexts). Fig. 10 shows an SEM image of the microstructure of the sintered Ti, TS-Ti, and Ti_H samples. The Ti and Ti_H samples displayed the maximum and minimum proportions of residual pores, respectively, which suggests that the densification degree of the TS-Ti sample is superior to the Ti sample and inferior to the Ti_H sample. Moreover, the densification degree of the three types of samples was confirmed by their relative densities, which were 97.0%, 98.2%, and 99.0% for samples Ti, TS-Ti, and Ti_H, respectively. Since only a self-purification effect was preserved to accelerate densification in the TS-Ti sample, the defects generation effect in the Ti_H sample promoted the powder densification process. Again, these results prove that dehydrogenation introduced extra defects into the sintered samples.

Unlike in pressure-assisted sintering, no extrinsic pressure is applied in pressureless sintering. The extrinsic pressure shortens the



Fig. 10. SEM images of the microstructures of the sintered Ti (a), TS-Ti (b), and Ti_{H} (c) samples.

distance and increases the contact area between powder particles, causing powder particles or sintered bulk materials to yield and creep at higher sintering temperatures, which is crucial for eliminating pores [30]. Usually, pressureless-sintered bulk Ti can not achieve nearly full-density, whose relative density is lower than 98%. Fortunately, applying TiH₂ as a starting material overcomes this problem. During industrial production, HDH-Ti powder is prepared by the dehydrogenation of TiH₂ powder. It seems that dehydrogenation may introduce a high concentration of crystal defects: however, the need for an unavoidable cooling stage can lead to the recovery of crystal defects (Fig. 9b); therefore, nearly no extra defects are persevered after cooling to ambient temperature. This was verified by the lack of an exothermic peak in the reheating curve in Fig. 9c. Despite the reduction in the O content due to self-purification after dehydrogenation, the HDH-Ti powder again absorbed considerable O contaminants during storage and pressing, resulting in the formation of a thick oxide layer on the powder surface. The above two aspects outline the limitation of the dehydrogenation effects. Consequently, applying TiH₂ powder as the sintering precursor can effectively circumvent limitations due to dehydrogenation effects, and is beneficial for accelerating powder densification and thus fabricating nearly full-density bulk Ti and Ti alloys with high mechanical properties.

5. Conclusions

The dehydrogenation and resultant densification mechanism were revealed by a designed two-step sintering strategy that included the pressureless sintering of a TiH₂ powder precursor. Compared with the HDH-Ti compact, the TiH₂ compact has the same sintering diffusion mechanism of grain boundary diffusion, a 53% lower sintering activation energy, and a 3% greater onset relative density of rapid grain growth. This led to a 2.3% higher relative density and 60 µm smaller grain size in the TiH₂ compact than the HDH-Ti compact. Interestingly, the bulk Ti sintered from the TiH₂ compact exhibited an ultimate strength of 659 MPa and 20.8% elongation, which were far superior to bulk Ti

Appendix A

The deformation gradient tensors of FCC-TiH₂ to HCP-Ti are calculated by method of Woo [61]. The two most common orientation relationships of FCC TiH₂→HCP Ti are expressed as OR1: $\{1\overline{1}1\}_{\delta}//\{0001\}_{\alpha} <110>_{\delta}$ // $\langle 1\overline{2}10>_{\alpha}$ and OR2: $\{001\}_{\delta}//\{0001\}_{\alpha} <110>_{\delta}$ // $\langle 1\overline{2}10>_{\alpha}$. As for OR1, the phase transformation is accomplished by the passage of $a/6 < \overline{1}\overline{1}2$ >partial dislocations on the {111} plane [63,64]. The

coordinate systems for this case is shown as follows:

 $\begin{aligned} \mathbf{x}_1 : [\bar{1}10]_{\delta} \to [2\bar{1}\bar{1}0]_{\alpha} \Rightarrow \sqrt{2}/2a_{\delta} \to a_{\alpha}. \\ \mathbf{x}_2 : [\bar{1}\bar{1}2]_{\delta} \to [01\bar{1}0]_{\alpha} \Rightarrow \sqrt{6}/2a_{\delta} \to \sqrt{3}a_{\alpha}. \\ \mathbf{x}_3 : [111]_{\delta} \to [0001]_{\alpha} \Rightarrow 2/\sqrt{3}a_{\delta} \to c_{\alpha}. \end{aligned}$

In dehydrogenation process, The FCC TiH₂ phase is first transformed to metastable FCT γ -hydride (TiH, a = 0.420 nm, c = 0.470 nm) followed by dilating to the FCC lattice with a = 0.417 nm, and then shearing $\sqrt{2}/4$ along $<\overline{112}>$ direction to change of stacking sequence ABC/AB, leading to HCP Ti generation.

The first step in calculation is to dilate the FCC lattice to FCT, the matrix for the step, referring to coordinate system index is:

materials obtained by various other processing approaches, especially sintered bulk Ti from HDH-Ti powder. Essentially, the excellent mechanical properties reported herein originated from accelerated densification and a decreased grain size, which were induced by 3% extra defects generated via dehydrogenation during sintering of the TiH₂ compact. This work reports the first quantification of the dehydrogenation effect and resultant densification mechanism during the pressureless sintering of TiH₂ powder, which can help produce Ti and Ti alloys with better mechanical properties for use as structural materials.

CRediT authorship contribution statement

T. Chen: Methodology, Investigation, Visualization, Writing. C. Yang: Writing-review & editing, Supervision, Funding acquisition, Project administration. Z. Liu: Investigation, Formal analysis. H.W. Ma: Formal analysis. L.M. Kang: Discussion. Z. Wang: Language polish. W.W. Zhang: Discussion. D.D. Li: Formal analysis. N. Li: Discussion. Y.Y. Li: Supervision, Discussion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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(A7)

where
$$A = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{6}} & \frac{-1}{\sqrt{3}} \\ \frac{-1}{\sqrt{2}} & \frac{-1}{\sqrt{6}} & \frac{-1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{6}} & \frac{-1}{\sqrt{3}} \end{bmatrix}$$
 (2).
and $T_1 = \begin{bmatrix} \xi_1 & 0 & 0 \\ 0 & \xi_1 & 0 \\ 0 & 0 & \xi_2 \end{bmatrix}$ (3).

with $\xi_1 = 0.420/0.444$, $\xi_2 = 0.470/0.444$.

The FCT lattice is further dilated to FCC lattice with a = 0.417 nm, where the deformation matrix is:

$$M_{2} = A^{-1}T_{2}A$$
(A4)
where $T_{2} = \begin{bmatrix} r_{1} & 0 & 0 \\ 0 & r_{1} & 0 \\ 0 & 0 & r_{2} \end{bmatrix}$ (5).

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with r_1 = 0.417/0.420, r_2 = 0.417/0.470.
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The FCC to HCP transformation was achieved by the passage of $a/6 < \overline{112}$ partial dislocations on the {111} plane, which is shearing $\sqrt{2}/4$ along $<\overline{112}$ direction followed by dilating the (c/a) ratio for Ti from 1.633 (the ideal value for HCP) to 1.588. The matrix for this step is:

$$M_{3} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & \sqrt{2}/4 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1.588/1.633 \end{bmatrix}$$
(A6)

Combining these three steps, the deformation gradient tensor of OR1 FCC TiH₂ \rightarrow HCP Ti transformation is:

 $B = M_1 M_2 M_3$

Which is calculated as:

$$B = \begin{bmatrix} 0.9392 & 0 & 0\\ 0 & 0.9392 & 0.3320\\ 0 & 0 & 0.9133 \end{bmatrix}$$
(A8)

The change of the transformation from FCC to HCP is obtained by the determinant of the strain matrix:

$$\frac{V_{HCP}}{V_{FCC}} = |B| = 0.806 \tag{A9}$$

Therefore, the volume change from FCC to HCP transition with OR1 is calculated by the formula $(V_{FCC} - V_{HCP})/V_{FCC}$ was about 19.4%. As for OR2, the phase transformation is accomplished via pure-shuffle mechanism. The stacking sequence for FCC and HCP lattice along <001> and <0001> direction is AB/AB, Thus, only atomic shuffle are considered in calculation. The coordinate systems selected in the current work are shown as follows:

 $\begin{aligned} \mathbf{x_1} : [1\overline{1}0]_{\delta} &\to [2\overline{1}\overline{1}0]_{\alpha} \Rightarrow \sqrt{2}/2a_{\delta} \to a_{\alpha}. \\ \mathbf{x_2} : [110]_{\delta} \to [01\overline{1}0]_{\alpha} \Rightarrow \sqrt{2}a_{\delta} \to \sqrt{3}a_{\alpha}. \\ \mathbf{x_3} : [001]_{\delta} \to [0001]_{\alpha} \Rightarrow a_{\delta} \to c_{\alpha}. \end{aligned}$

The first step is FCC lattice transformed to metastable FCT lattice with atomic shuffle, in which the matrix can be expressed as:

	<i>s</i> ₁	0	0]	
$P_1 =$	0	<i>s</i> ₁	0	
	0	0 :	s ₂	(A10)

with s1 = 0.420/0.444, and s2 = 0.470/0.444. The lattice matrix transformed from FCT to HCP in the second step is:

	t_1	0	0]	$\sqrt{2}$	0	0]	
$P_2 =$	0	t_1	0	0	$\sqrt{6}/2$	0	
	0	0	t_2	0	0	1	(A11)

with $t_1 = 0.295/0.420$, and $t_2 = 0.468/0.470$.

Combining these two steps, the deformation gradient tensor of OR2 FCC-TiH₂ \rightarrow HCP-Ti transformation is:

$C = P_1 P_2$	(A12)
which is calculated as:	

$C = \begin{bmatrix} 0.9 \\ 0.9 \end{bmatrix}$	9396	0	0
	0	0.8137	0
	0	0	1.0541

The change of the transformation from FCC to HCP is obtained by the determinant of the strain matrix:

$$\frac{V_{HCP}}{V_{ECC}} = |C| = 0.806$$

(A14)

Therefore, the volume change from FCC to HCP transition with OR2 is calculated by the formula $(V_{FCC} - V_{HCP})/V_{FCC}$ was about 19.4%.

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