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Highlights

- Dense Ti-Al-Nb alloy is cost-effectively fabricated by TiH_2 -assisted pressureless sintering.
- Quasi-static and dynamic compressive strengths are improved by TiH_2 -assisted sintering.
- Densification mechanism is elucidated by in situ LSCM observation.
- Phase transformations over the sintering process are revealed.

Research Article

In situ investigation on densification mechanism of Ti-20Al-19Nb (at.%) alloy by TiH₂-assisted pressureless sintering

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Abstract

Dense Ti-20Al-19Nb (at.%) alloys can be cost-effectively fabricated by TiH₂-assisted pressureless sintering; nevertheless, the densification mechanism remains controversial without understanding the entire sintering process. By in situ observing the surface morphology of the Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts upon heating, the densification mechanism of the Ti-20Al-19Nb alloys was elucidated in this study. In addition to the reported reason that the dehydrogenation of TiH₂ provided reactive Ti, the densification of Ti-20Al-19Nb alloy was found to be strongly associated with the phase transformations upon sintering. The TiH₂ participated in the reverse eutectoid transformation, $\alpha\text{-Ti} + \delta\text{-TiH}_2 \rightarrow \beta\text{-Ti}$, inducing the α/β and TiH₂/ β grain boundaries for the rapid diffusion of Al. The reaction of $\text{Ti(s)} + \text{Al(s)} \rightarrow \text{TiAl}_3\text{(s)}$ was then accelerated, and the

majority of the Al phase was consumed in the solid state, which significantly reduced the pores from the transient liquid Al. The activation energy of the Ti-Al reaction decreased with the addition of TiH_2 , and the growth mode of the TiAl_3 phase was changed. By removing the large pores at 700 °C, the Ti-Al intermetallic phases were well connected, forming the continuous interdiffusion route for Ti, Al, and Nb. The diffusion of Nb, as well as the phase transformation of $\alpha_2 \rightarrow \text{B2}$, was then promoted, and the ripening time for the B2 phase was increased. As a result, the density and mechanical properties were improved. The initial results of this study provided a foundation for the cost-effective fabrication of high-strength Ti-Al alloys containing refractory elements.

Keywords: Ti-Al-Nb alloy; Sintering mechanism; Porosity; In situ observation; Phase transformation

1. Introduction

Ti-Al-Nb alloys, which possess high strength and excellent corrosion resistance, have been the focus of worldwide attention due primarily to their potential for aerospace applications [1–3]. Although considerable progress has been achieved, the potential of Ti-Al-Nb alloys for replacing the nickel-based superalloys in the engine parts remains limited by the difficulties in smelting and processing [4], as the melting points, densities, and vapor pressures of the Ti, Al, and Nb elements differ significantly. For a $\text{Ti}_{44}\text{Al}_{48}\text{Nb}_8$ alloy with low Nb content, the large-scale components with desired shapes were prepared by the electromagnetic levitation method and pressure die-casting [5, 6]. However, the Ti-(18-30)Al-(12.5-30)Nb (at.%) alloys with high Nb content may contain intermetallic phases of Ti_3Al (α_2) and Ti_2AlNb (O) with a high alloying degree, and element segregation will occur during smelting. As far as the deformation processing, harsh conditions are

required for Ti-22Al-25Nb alloys with intrinsic brittleness [7]. Large-tonnage forging and rolling equipment are required even for small-sized Ti-22Al-25Nb workpieces, and the thermal processing window is narrow due to the sensitivity of the microstructure and properties to heat response. As a result, powder metallurgy, a near-net-shape technique, was employed to fabricate uniform and shaped Ti-22Al-25Nb components by researchers. Among the common powder metallurgy methods, spark plasma sintering (SPS) and hot isostatic pressing (HIP) have been widely used to prepare Ti-22Al-25Nb and Ti-22Al-24Nb-0.5Mo (at.%) alloys [8–10]. These two methods are both pressure-assisted. A Ti-22Al-25Nb (at.%) alloy was rapidly SPSed under 50 MPa by Niu et al. [11], and a yield strength of 1220 MPa was obtained at room temperature by modifying the morphology of the orthorhombic phase. The advantage of the SPS method is high efficiency, whereas the disadvantage is the heterogeneity of the microstructure, including the undissolved Nb particles or pores. For instance, niobium particles were partially diffused, when the Ti-48Al-2Cr-2Nb (at.%) alloy was synthesized by SPS at 1300 °C and 50 MPa [12]. A similar phenomenon was also observed in the Ti-22Al-25Nb (at.%) sintered at 1150 °C and 35 MPa [13]. Moreover, hot-packed rolling was commonly required to remove the sintering pores of the Ti-20.3Al-24.7Nb (at.%) prepared by SPS [14]. In contrast, the HIPed alloy was sintered under a higher pressure to guarantee the homogeneity of the microstructure and the strength. Zhang et al. [15] sintered a Ti-22Al-23.9Nb-1.1Mo (at.%) alloy under 120 MPa by HIP, and the alloy exhibited a strength of 900 MPa and an elongation to failure of 4.7% at 650 °C. To improve the elongation to failure of the Ti-22Al-26Nb (at.%) alloy, a large amount of Nb or other refractory elements were incorporated, and the applied pressure was up to 207 MPa for HIP [16]. However, pores still existed in the sintered alloys.

For Ti-(18-30)Al-(12.5-30)Nb (at.%) alloys, the raw materials were normally the costly pre-

alloyed powders when the SPS and HIP methods were used. With the continuous progress in powder metallurgy, researchers intended to fabricate high-density structural materials with a low production cost [17]. On the one hand, the use of elemental powders instead of pre-alloyed powders could significantly reduce the cost of raw materials. On the other hand, using pressureless sintering instead of pressure-assisted sintering complied with the concept of energy conservation. However, high porosity was the main drawback for the pressureless-sintered Ti-12Al-41.2Nb (wt.%) alloys [18] and powder metallurgic Ti-49Al (at.%) alloys [19, 20], which might result in inferior mechanical properties. Recently, a dense Ti-22Al-17.5Nb (at.%) alloy was fabricated from Al-Nb master alloy powders by pressureless sintering, and its tensile strength was improved at room temperature and 600 °C compared with that of the alloy prepared from pure Al powder [21]. With the intense development of the Ti-Al-Nb alloy, the refractory Ta, Mo, and Hf elements were incorporated to regulate the proportion and morphology of the intermetallic phases [22]. However, the preparation of Al-Ta, Al-Mo, and Al-Hf intermediate alloys is complex. Due to the unavailability of these intermediate alloys, elemental materials are still used to prepare Ti-Al-Nb-Ta/Mo/Hf alloys, and the above-mentioned method is not suitable for densification.

Previous studies showed that TiH_2 played an essential role in increasing the density of the sintered pure Ti, TC4, Ti-5553, and Ti-1023 alloys by powder metallurgy [23, 24]. Mei et al. [25] compared the density and mechanical properties of the pure Ti samples sintered from elemental Ti powder and TiH_2 powder, respectively. The shrinkage of the TiH_2 green compact was larger than that of the pure Ti compact after sintering. Accordingly, the density and the compressive strength were improved. In addition, the content of oxygen in the TiH_2 -prepared sample was lower than that of the one from pure Ti powder [26]. Wang et al. [27] suggested that the released H atoms reduced

the oxide film on the Ti particles, and the dehydrogenation-induced defects increased the reactivity of the Ti. When the TiH_2 was used to fabricate the Ti alloy containing Al, Ivasishin et al. [28] stated that the brittle TiH_2 was easily broken into flakes during ball milling, and the dehydrogenation-induced defects accelerated the reaction between Ti and Al, producing dense Ti-6Al-4V alloys by powder metallurgy. The TiH_2 was also used to fabricate dense Ti alloy containing refractory metal elements. Sharma et al. [29, 30] declared that a fine microstructure and excellent mechanical properties were obtained in a Ti-40Nb (wt.%) alloy prepared from TiH_2 powder. Wang et al. [31] fabricated the Ti-23Al-17Nb (wt.%) alloy with a high relative density (98.7%) by pressureless sintering from TiH_2 powder and Al-Nb master alloy powder. The authors demonstrated that the partial-alloying and cleansing effect of TiH_2 facilitated the densification process. Kayani et al. [32] proposed that the porosity in the $\text{Ti}_{52}\text{Al}_{48}$ alloy was determined by the extent of exothermic reactions during sintering, including $5\text{Ti} + 2\text{Al} \rightarrow \text{Ti}_2\text{Al}_3$ and $\text{Ti}_2\text{Al}_3 + \text{Al} \rightarrow 2\text{TiAl}_3$.

Up to now, the densification of the sintered Ti alloy was attributed to the highly-reactive Ti, originating from either the dehydrogenated TiH_2 or the exposed Ti, on which the Ti-O film was removed by H. Nevertheless, the densification mechanism remained controversial without understanding the phase transformations over the entire sintering process. Moreover, the mechanism was not investigated using in situ observation and characterization. Considering that the TiH_2 was conducive to the cost-effective manufacturing of the Ti-Al-Nb alloy, understanding the densification mechanism was of great significance in optimizing the sintering process for a high-quality alloy.

In this study, we first confirmed the role of TiH_2 in improving the density and mechanical properties of the pressureless-sintered Ti-20Al-19Nb (at.%) alloy. Then, the sintering processes of the Ti, Ti/ TiH_2 , Ti/Al, Ti/ TiH_2 /Al, Ti/Al/Nb, and Ti/ TiH_2 /Al/Nb systems were systematically

investigated by in situ characterizing the phase transformations and observing the microstructure evolution. By thermodynamic and kinetic analysis of the key phase transformation processes that affect porosity, the densification mechanism of the Ti-20Al-19Nb alloy was elucidated. This study provides guidance for optimizing the sintering procedure of Ti-20Al-19Nb alloys by pressureless sintering, and this method is expected to be used in other Ti alloys for cost-effective production.

2. Experimental details

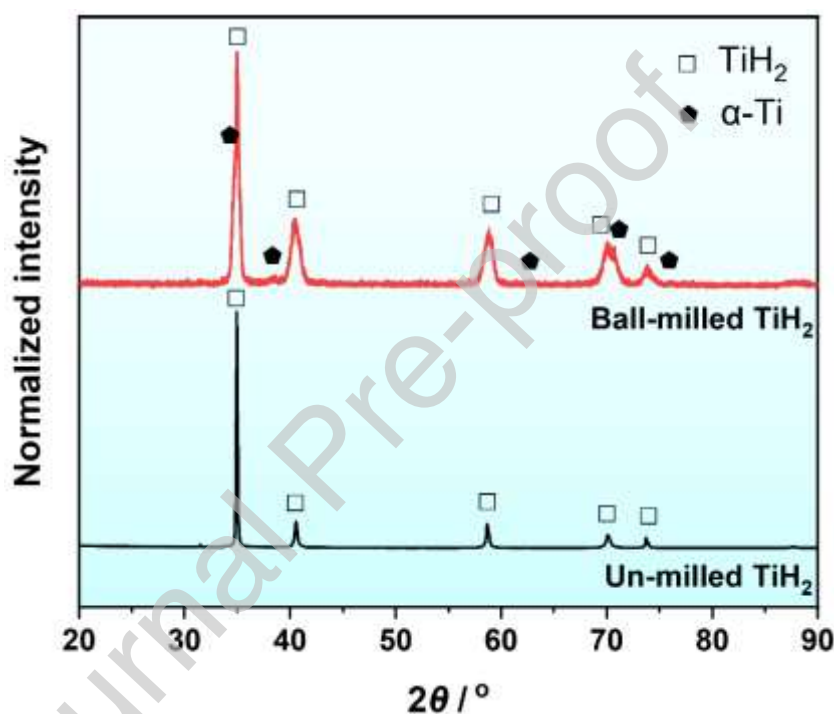


Fig. 1. XRD patterns of the un-milled and ball-milled TiH_2 powders.

The Ti-Al-Nb alloy (THAN#2) with a nominal composition of Ti-20Al-19Nb (at.%) was prepared from TiH_2 ($\sim 45 \mu\text{m}$, 99.6% in purity), Ti ($\sim 45 \mu\text{m}$, 99.9% in purity), Al ($\sim 5 \mu\text{m}$, 99.9% in purity), and Nb ($5\text{--}30 \mu\text{m}$, 99.9% in purity) powders. The Ti and TiH_2 powders were supplied by Guoheng Technology Chengdu Co., Ltd., and the Al and Nb powders were supplied by Beijing Xingrongyuan Technology Co., Ltd. The XRD pattern of the TiH_2 powder is shown in Fig. 1. The powder was composed of a single $\delta\text{-TiH}_2$ phase. A reference alloy (TAN#1) in the same nominal

composition was prepared from Ti ($\sim 45\ \mu\text{m}$, 99.9% in purity), Al ($\sim 5\ \mu\text{m}$, 99.9% in purity), and Nb ($5\text{--}30\ \mu\text{m}$, 99.9% in purity) powders. The SEM images of the raw materials are shown in Fig. 2. The Ti, TiH_2 , and Nb powders are in irregular shape, and the Al powder is spherical. The oxygen content of the raw materials was provided by the suppliers, which was $\leq 0.15\ \text{wt.}\%$ in Ti, $\leq 0.30\ \text{wt.}\%$ in TiH_2 , $\leq 0.20\ \text{wt.}\%$ in Al, and $\leq 0.30\ \text{wt.}\%$ in Nb, respectively. The powders were mixed in a planetary ball mill at $240\ \text{r min}^{-1}$ for 40 min, and the ball-to-powder weight ratio was 5:1. The TiH_2 powder was ball-milled separately to confirm its phase constituent in the mixture, and $\delta\text{-TiH}_2$ and $\alpha\text{-Ti}$ phases were found in the ball-milled TiH_2 powder, as shown in Fig. 1. Fig. 2(e–h) shows the SEM image of the mixed powder and corresponding element mappings for the Ti, TiH_2 , Al, and Nb powders. Those for the Ti, Al, and Nb powders have been shown in our previous studies [21]. The Al particles remained in their original morphology, and they adhered to the Ti and Nb particles. The Ti particles were milled into a sheet-like shape. Cold welding might be caused as signals of the Nb and Al elements were examined on the Ti particles (Fig. 2(f–h)). Under these conditions, the powders were mixed uniformly.

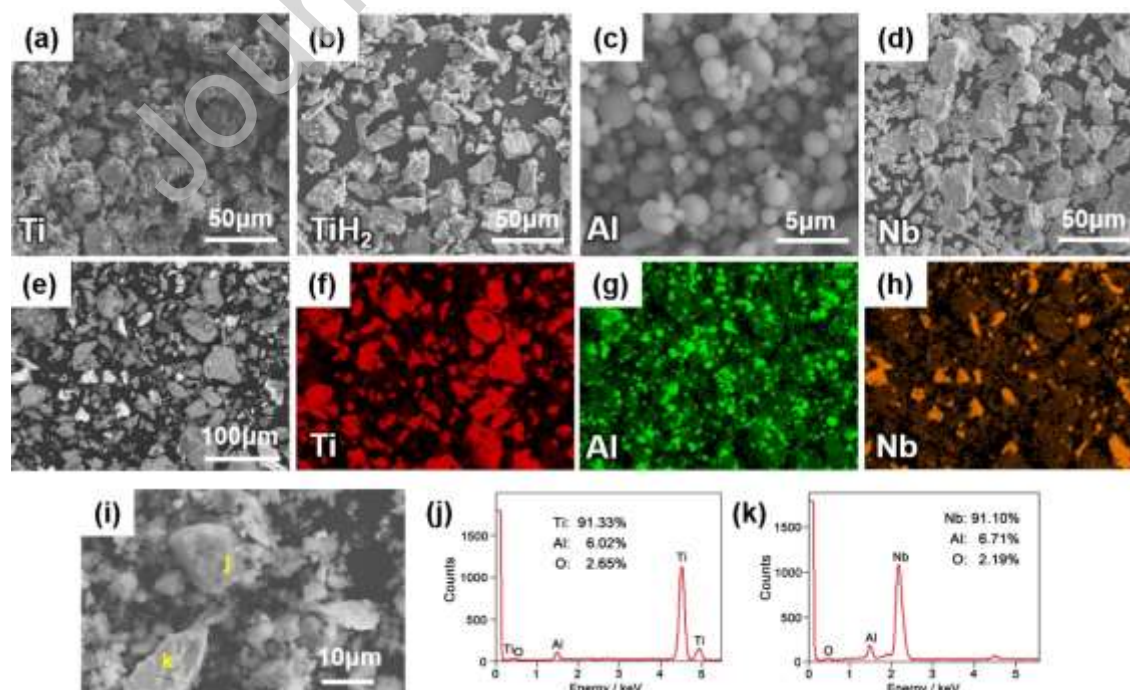


Fig. 2. SEM images of raw materials (a) Ti, (b) TiH₂, (c) Al, and (d) Nb powder. (e) SEM image of Ti, TiH₂, Al, and Nb mixed powders ($\times 300$), and (f–h) corresponding element mappings. (i) SEM image ($\times 2000$) of mixed powders. (j, k) EDS patterns of the regions in (i).

Then, the mixture was pressed by cold isostatic pressing at 250 MPa for 20 min to obtain the Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts with the dimension of $\Phi 15 \text{ mm} \times 120 \text{ mm}$. In the compacts containing TiH₂, the atomic ratio of Ti: TiH₂ was 1:1. The compacts were sintered at 1400 °C for 4 h with a heating rate of 10 °C min⁻¹ in a pipe furnace (Tianjin Zhonghuan SK-G10163) under Ar atmosphere, and the THAN#2 and TAN#1 alloys were obtained. The actual composition was measured by a P400-type inductively coupled plasma (ICP) emission spectrometer, and the oxygen content was examined by inert gas fusion-infrared/thermal conductivity analysis (IGA). The actual compositions of the sintered THAN#2 and TAN#1 alloys are shown in Table 1. The phase constituent of the bulk samples ($\Phi 10 \text{ mm} \times 10 \text{ mm}$) was examined by X-ray diffraction (Bruker D8 Advance) with Cu K α radiation ($\lambda = 0.15406 \text{ nm}$). The volume percentages of the phases were calculated using the intensity of the peaks on the XRD patterns. For instance, the volume percentage of the α_2 phase was obtained by dividing the sum of peak intensities that represent the α_2 phase by the sum of total peak intensities on the XRD pattern. The density of the alloys was measured by the Archimedes drainage method on an electronic analytical balance (AL204-IC). The specimens for microstructure observation were mechanically ground with increasing grades of SiC abrasive papers and polished with Fe₂O₃-H₂O solution and Cr₂O₃-H₂O solution in sequence. The microstructures of the specimens were then observed by scanning electron microscope (SEM, GeminiSEM 300). The quasi-static compression and tensile properties were measured by the universal electronic material testing machine (CMT4305), and the strain rate was 10⁻³ s⁻¹. The

dimension of the specimens for compression tests was $\Phi 5 \times 5$ mm, and the gauge length of the specimens for tensile tests was 40 mm with a diameter of 5 mm. The displacement was measured by laser extensometers. The dynamic compression properties of the specimens ($\Phi 4$ mm $\times$ 4 mm) were measured by the split Hopkinson pressure bar system, and the average strain rate was 4000 s^{-1} . The striker bar was driven by high-pressure nitrogen gas to impact the incident bar, and an incident wave was produced. When the incident bar impacted the specimen that was attached to the transmission bar, a portion of the incident wave was reflected to form a reflected wave, and the rest of the incident wave penetrated the specimen to form a transmission wave. The voltage of the strain gauges on the incident and transmission bars changed due to the strain. These voltage pulse signals were collected by a dynamic strain gauge and amplified in the data acquisition system. The incident strain $\varepsilon_i(t)$, reflected strain $\varepsilon_r(t)$, and transmitted strain $\varepsilon_t(t)$ were obtained, and the stress $\sigma(t)$, strain $\varepsilon(t)$, and strain rate $\dot{\varepsilon}(t)$ were calculated by the following equations [33].

$$\sigma(t) = (A_B E_B / 2A_s) [\varepsilon_i(t) + \varepsilon_r(t) + \varepsilon_t(t)] \quad (1)$$

$$\varepsilon(t) = (C_e / L_s) \int_0^t [\varepsilon_i(t) - \varepsilon_r(t) - \varepsilon_t(t)] dt \quad (2)$$

$$\dot{\varepsilon}(t) = (C_e / L_s) [\varepsilon_i(t) - \varepsilon_r(t) - \varepsilon_t(t)] \quad (3)$$

where A_B and E_B are the cross-sectional areas and Young's modulus of the bar, respectively, A_s and L_s are the cross-sectional area and length of the specimen, respectively, C_e is the elastic wave velocity in the bar, and t is the time.

Table 1. Actual compositions of the sintered TAN#1 and THAN#2 alloys.

Actual composition	Ti	Al	Nb	O
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TAN#1/wt.%	Bal.	10.21	33.63	0.65
TAN#1/at.%	Bal.	19.5	18.6	2.1
THAN#2/wt.%	Bal.	10.81	33.52	0.60
THAN#2/at.%	Bal.	20.6	18.8	1.9

The densification mechanism was investigated by the following methods. Pure Ti, Ti/TiH₂, Ti/Al, Ti/TiH₂/Al, Ti/Al/Nb, and Ti/TiH₂/Al/Nb compacts ($\Phi 15$ mm $\times$ 150 mm) were prepared by cold isostatic pressing at 250 MPa for 20 min. The nominal composition of the Ti/Al and Ti/TiH₂/Al compacts was Ti-25Al (at.%), and that of the Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts was Ti-20Al-19Nb (at.%). In the compacts containing TiH₂, the atomic ratio of Ti: TiH₂ was 1:1. Cylindrical specimens ($\Phi 6$ mm $\times$ 4 mm) were cut from the compacts, and the surface morphologies of these specimens were *in situ* observed by the laser scanning confocal microscope (LSCM, Lasertec VL2000DX-SVF17SP) from 20 °C to 1400 °C with the heating rate of 10 °C min⁻¹. Before the LSCM observation, the specimens were mechanically ground and polished by the above-mentioned method. The Ti/Al and Ti/TiH₂/Al compacts were heated up to 1200 °C in a differential scanning calorimeter (DSC, Mettler Toledo TGA/DSC 3+) at a heating rate of 10, 20, and 30 °C min⁻¹ under Ar atmosphere, and the thermal signals upon sintering were recorded synchronously. Using the thermogravimetry (TG) apparatus (Mettler Toledo TGA/DSC 3+), the TG curves of the Ti and Ti/TiH₂ compacts were measured from 25 °C to 1000 °C under Ar atmosphere, and the weight loss of TiH₂ due to dehydrogenation was studied. Meanwhile, the phase transitions upon sintering were examined by *in situ* X-ray diffraction (Bruker D8 Advance) from 25 °C to 600 °C. Quenching experiments were performed to confirm the phase transformations and microstructure evolution at high temperatures. The Ti/Al, Ti/TiH₂/Al, Ti/Al/Nb, and TiH₂/Al/Nb specimens ($\Phi 5$ mm $\times$ 5 mm) were sealed in vacuum quartz tubes, and heated up to 500, 600, 700, 800, 900, 1000, 1100, and

1200 °C with a rate of 10 °C min⁻¹. Then the compacts were quenched at these temperatures to “freeze” the high-temperature phase and microstructure to room temperature. The phase constituent and microstructure were characterized by XRD (Bruker D8 Advance) and SEM (GeminiSEM 300), respectively. A transmission electron microscope (TEM, FEI Tecnai G2 F20) equipped with energy dispersive spectroscopy (EDS, Bruker XFlash 5030) was used to confirm the formed intermetallic phases during sintering, and the used accelerating voltage was 200 kV. The foil for TEM observation was prepared by a focused ion beam (FIB, FEI Helios G4) from the Ti/TiH₂/Al/Nb compact quenched at 800 °C. To protect the foil from possible damage, a Pt layer was deposited on the surface of the foil. After thinning and cleaning by the beam, a foil of about 100 nm thick was obtained for the TEM observation. The thermodynamic analysis was based on the CALPHAD (Calculation of Phase Diagrams) method. The kinetics of the key reaction that affected the porosity were analyzed by a multi-rate scanning Flynn–Wall–Ozawa method [34, 35].

3. Results and discussion

3.1. Characterization of Ti-20Al-19Nb alloys prepared from Ti powder and TiH₂ powder

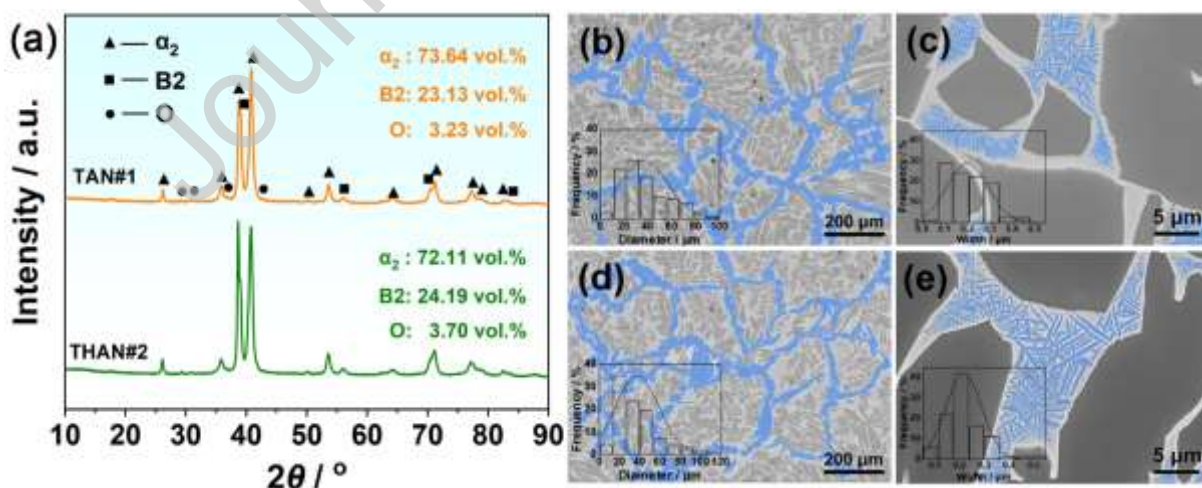


Fig. 3. (a) XRD patterns of TAN#1 and THAN#2 alloys. Backscattered electron (BSE) images of TAN#1 (b) $\times 100$, and (c) $\times 3000$. BSE images of THAN#2 (d) $\times 100$, and (e) $\times 3000$. Insets of (b)

and (d) are frequency distributions of the dimensions of the grain boundary α_2 for TAN#1 and THAN#2, respectively. Insets of (c) and (e) are frequency distributions of the dimensions of the acicular O for TAN#1 and THAN#2, respectively.

Fig. 3(a) shows the XRD patterns of the Ti-20Al-19Nb alloys prepared from Ti powder (TAN#1) and TiH₂ powder (THAN#2). The alloys both contained α_2 , B2, and O phases, among which the α_2 phase was the main phase. The volume percentages of the three phases are shown in Fig. 3(a) for the TAN#1 and THAN#2 alloys. The TAN#1 alloy was composed of 73.64 vol.% α_2 , 23.13 vol.% B2, and 3.23 vol.% O phase. Compared with the TAN#1 alloy, the volume percentages of the three phases in the THAN#2 alloy fluctuated within a narrow range, and the values were 72.11 vol.%, 24.19 vol.%, and 3.70 vol.% for the α_2 , B2, and O phase, respectively. Fig. 3(b–e) shows the backscattered electron (BSE) images of the TAN#1 and THAN#2 alloys sintered at 1400 °C. The microstructure of the two alloys featured grain boundary α_2 , equiaxed α_2 , and acicular O phase on the B2 matrix. As shown in Fig. 3(b, d), the grains of the matrix phase appearing dark grey were fully or partially surrounded by the α_2 phase colored blue. Such behavior is similar to the incomplete wetting of the β -Ti grain boundaries by the second solid phase α -Ti in the Ti-Fe and Ti-Co alloys [36, 37]. The interlayers of the second phase at the grain boundaries would strongly influence the overall mechanical properties [38]. The microstructure of the powder metallurgic Ti-20Al-19Nb alloy differed from the as-cast Ti-Al-Nb alloys of similar compositions. Boehlert et al. [39, 40] have reported that the as-cast microstructure of the Ti-25Al-25Nb and Ti-23Al-27Nb contained lenticular O phase and α_2 platelets inside prior B2 grains. The complete and incomplete wetting of grain boundaries by the second solid phase was hardly found in those as-cast alloys. The Ti-12Al-38Nb contained a single β phase, and the β grains were as large as 500 μm .

The volume percentages of each phase were obtained by calculating the area ratios of each phase region with respect to the image, and those for the α_2 , B2, and O phases were 74.70 vol.%, 20.84 vol.%, and 4.46 vol.%, respectively. Compared with the values obtained by the Rietveld method, the deviation in the volume percentage was less than 4% for these three phases. The frequency distributions of the dimensions of the grain boundary α_2 and acicular O are shown in the insets of Fig. 3(b–e). The average size of the grain boundary α_2 was 36.84 μm and 37.82 μm in the TAN#1 and THAN#2 alloy, respectively, and that of the acicular O was 0.21 μm and 0.20 μm in the TAN#1 and THAN#2 alloy, respectively. Overall, the phase constituent and the microstructure hardly changed between the TAN#1 and THAN#2 alloys.

The BSE images focusing on the pores are shown in Fig. 4(a, b) for the TAN#1 and THAN#2 alloys, respectively. The TAN#1 alloy contained pores with an average diameter of $11.31 \pm 0.86 \mu\text{m}$, and the porosity reached 5.34% (Fig. 4(a)). The THAN#2 alloy contained refined pores with an average diameter of $6.11 \pm 0.64 \mu\text{m}$, and the porosity was reduced to 0.86% (Fig. 4(b)). Using the Archimedes drainage method, the densities of the TAN#1 and THAN#2 alloys were measured to be 4.63 g cm^{-3} and 4.82 g cm^{-3} , respectively. Hence, the use of TiH_2 was conducive to the densification of the Ti-20Al-19Nb alloy by pressureless sintering. Fig. 4(e, f) shows the quasi-static and dynamic engineering compressive stress–strain curves, respectively, of the TAN#1 and THAN#2 alloys at room temperature. Under the quasi-static condition, the yield strength and the engineering strain-to-failure of the TAN#1 alloy were 874 MPa and 0.44, respectively. In contrast, the yield strength increased by 22% (1064 MPa), while the strain-to-failure decreased by 27% (0.32) for the THAN#2 alloy. Under the dynamic condition, the yield strength and strain-to-failure of the TAN#1 alloy were 1036 MPa and 0.37, respectively. Analogous to the variation tendency in the static strength and

plasticity, the yield strength increased to 1182 MPa, while the strain-to-failure decreased to 0.37 for the THAN#2 alloy. The SEM images of the longitudinal sections are shown in Fig. 4(c, d) for the THAN#2 specimens that experienced quasi-static and dynamic compression, respectively. The cracks initiated in the α_2 phase and terminated at the α_2 /B2 interfaces. Hence, when the B2 grain boundaries were completely wetted, cracks were prone to propagate along the grain boundaries and caused the fracture. In contrast, the incomplete wetting of the B2 grain boundaries is beneficial to prevent crack propagation. Under the tensile condition, both specimens showed the feature of brittle fracture. The tensile strength and the elongation-to-failure of the TAN#1 specimen were 670 MPa and 0.009, respectively, and those of the THAN#2 specimen were 926 MPa and 0.016, respectively (Fig. 4(g)). The tensile strength and elongation-to-failure are enhanced by TiH₂-assisted sintering. Boehlert [41] has systematically investigated the tensile properties of the Ti-Al-Nb alloys of similar compositions. The Ti-25Al-24Nb alloys of fully-B2 or fully-O microstructure were brittle and failed at less than 0.010 and 700 MPa. In contrast, the powder metallurgic Ti-20Al-19Nb of multiphase microstructure possesses a higher tensile strength, and the elongation-to-failure is slightly improved. Moreover, the as-processed Ti-22Al-24Nb alloy by induction-float-zone melting exhibited a tensile strength of 916 MPa and an elongation-to-failure of 0.045. The powder metallurgic Ti-20Al-19Nb alloy showed a comparable tensile strength but a low elongation-to-failure.

When the TAN#1 and THAN#2 specimens were subjected to tensile stress, they exhibited brittle fracture behavior without apparent plastic deformation, as the elongation-to-failure was less than 0.020. Under the tensile condition, stress concentrations around the pores led to the initiation and propagation of cracks. For the THAN#2 alloy, the decrease in porosity is beneficial to

increasing the strength and elongation-to-failure of the specimen. When the TAN#1 and THAN#2 specimens were subjected to compressive stress, plastic deformation occurred before fracture. The closure of the pores in the specimens was synchronized with the plastic deformation, and these pores can accommodate the deformation in a coordinated manner under external load, without causing premature failure [42]. Therefore, the fracture-to-strain of the TAN#1 alloy containing large-sized pores was larger than that of the THAN#2 alloy under compression. To sum up, besides the densification, the TiH_2 was also advantageous to the quasi-static compression strength, dynamic compression strength, and tensile properties of the Ti-20Al-19Nb alloys by pressureless sintering.

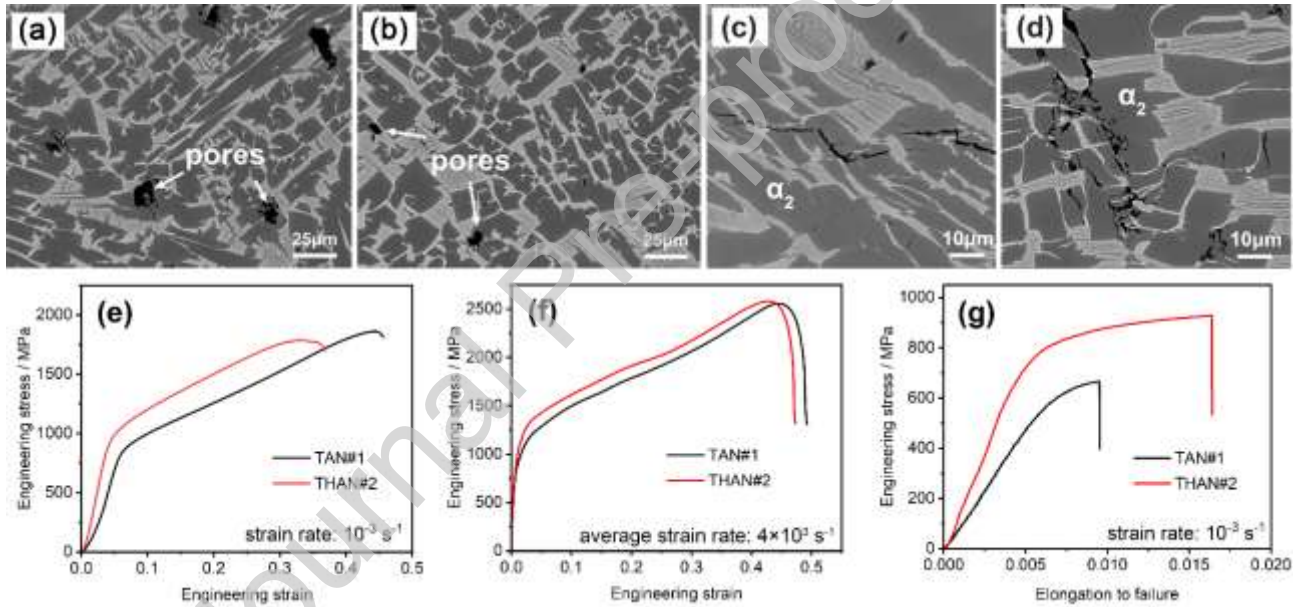


Fig. 4. BSE images ($\times 500$) of (a) TAN#1 and (b) THAN#2 alloys. Fracture morphology of THAN#2 alloy after (c) quasi-static and (d) dynamic compression. (e) Quasi-static compression, (f) dynamic compression, and (g) tensile stress–strain curves of TAN#1 and THAN#2 alloys.

3.2. Densification mechanism of Ti-20Al-19Nb alloy prepared by TiH_2 powder

3.2.1. *In situ* observation of Ti and TiH_2 compacts upon heating

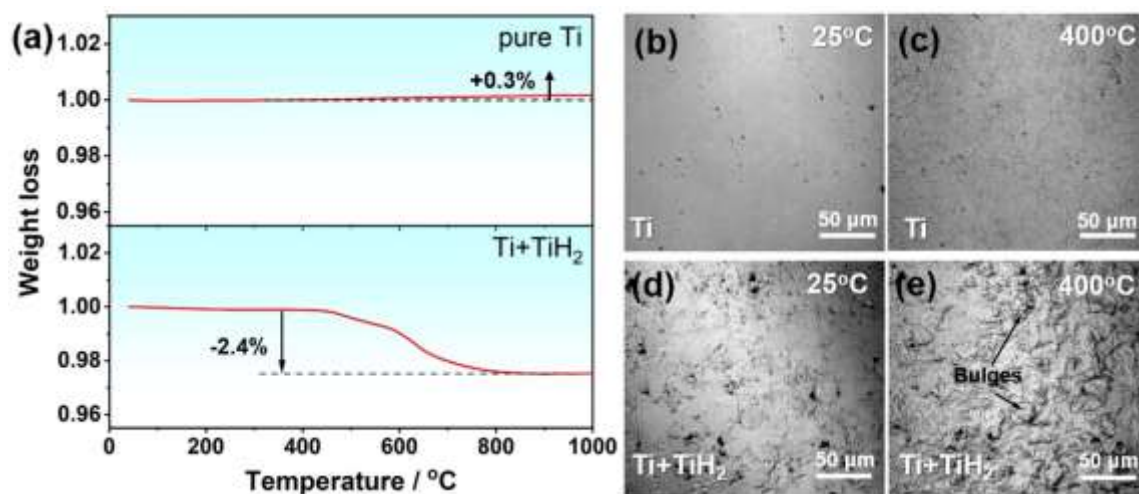


Fig. 5. (a) Thermogravimetry (TG) profile of Ti and Ti/TiH₂ compacts. Typical high-resolution LSCM images of pure Ti compacts at (b) 25 °C and (c) 400 °C. LSCM images of Ti/TiH₂ compacts at (d) 25 °C and (e) 400 °C.

The thermogravimetry (TG) profiles of the Ti and Ti/TiH₂ compacts during the heating process are shown in Fig. 5(a). The weight of the pure Ti compact increased by 0.3% as the temperature increased to 1000 °C due to the oxidation of Ti. On the contrary, the weight of the Ti/TiH₂ compact successively decreased by 2.4% when the temperature increased from 25 °C to 800 °C. The initial temperature for the noticeable weight loss was about 400 °C, and the possible reason was the dehydrogenation of TiH₂. The LSCM micrographs of the Ti and Ti/TiH₂ compacts at 25 °C and 400 °C are shown in Fig. 5(b, e), and the videos are shown in Supplementary Materials S1 and S2. The surface of the pure Ti compact remained flat upon heating, while bulges appeared on the surface of the Ti/TiH₂ compact when the temperature increased to 400 °C (Fig. 5(e)), which was just the temperature that the obvious weight loss initiated (Fig. 5(a)). Therefore, the bulges might be attributed to the dehydrogenation of TiH₂ that induced lattice distortion. To figure out the reason for the lattice distortion, the binary phase diagram of the Ti-H system at 1 atm was reproduced based on the data of Wang et al. [43] (Fig. 6(a)). The slowly released H was dissolved in the α -Ti crystals

upon heating, forming the α -Ti solid solution containing H. A reverse eutectoid transformation, α -Ti + δ -TiH₂ $\rightarrow$ β -Ti, occurred at 313 °C in equilibrium. The formed β -Ti phase was also a solid-solution phase containing H. The dissolved H would lead to the lattice distortion in the α -Ti and β -Ti crystals. The *in situ* XRD examination was employed to investigate the phase transformation and the changes in the lattice parameters upon heating in the Ti and Ti/TiH₂ systems. Refractory Mo was incorporated to calibrate the peak position, and the *in situ* XRD patterns for the Ti/Mo and Ti/TiH₂/Mo compacts are shown in Fig. 6(b), in which the peak of the Mo phase remained unchanged as the temperature increased. For the Ti/Mo compact, the characteristic peaks of the (101)_{Ti} and (002)_{Ti} crystal face gradually shifted to low angles since the crystal of Ti expanded with the increasing temperature. The shifting angles for the (101) and (002) crystal faces were 0.28° and 0.34°, respectively, from 25 °C to 600 °C, and no characteristic peaks of other phases appeared. For the Ti/TiH₂/Mo compacts, the shifting angles of (101)_{Ti} and (002)_{Ti} characteristic peaks from 25 °C to 600 °C were 0.60° and 0.77°, respectively, which are more than twice that of the angles for the Ti/Mo compact. Due to the solid solution of H, the lattice expansion of α -Ti was more severe in the presence of TiH₂. Meanwhile, the characteristic peak of the β -Ti phase appeared at $2\theta = 38.4^\circ$ under a temperature higher than the theoretical temperature of the $\alpha \rightarrow \beta$ phase transformation, which proved that the occurrence of the inverse eutectoid transformation α -Ti + δ -TiH₂ $\rightarrow$ β -Ti. Hence, the dehydrogenation of TiH₂ and the severe lattice expansion of α -Ti led to the rough surface of the Ti/TiH₂ compact upon heating. The maximum solubility of H in β -Ti is 50.8% in mole fraction. The peak position of the β phase remained unchanged due to the possible temporary saturation of Ti particles with hydrogen released from TiH₂ particles. In principle, the defect-containing Ti particles are more reactive than the pure Ti powder in reacting with Al or Nb particles.

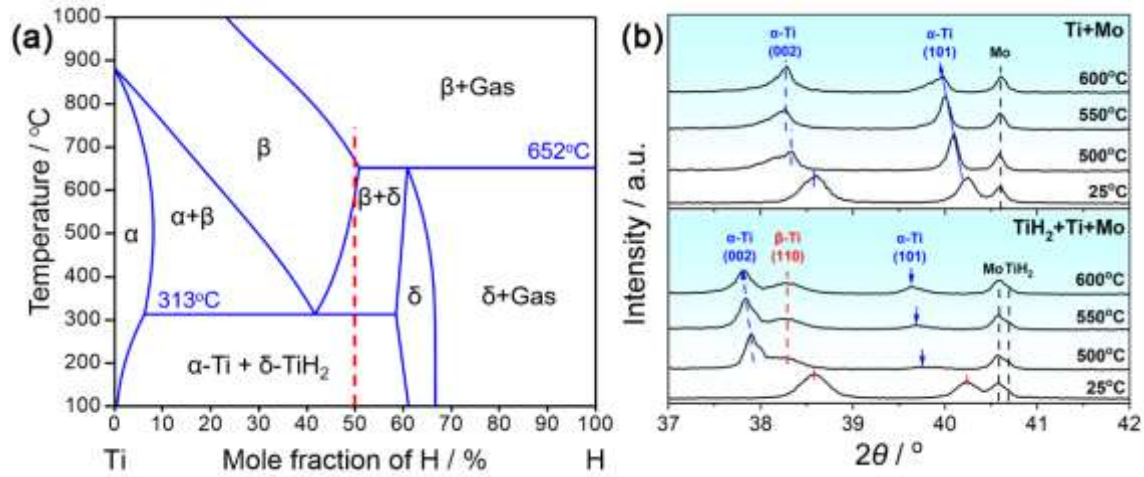


Fig. 6. (a) Reproduced phase diagram of the Ti–H system at 1 atm [43]. (b) *In situ* XRD patterns of Ti/Mo and Ti/TiH₂/Mo compacts.

3.2.2. *In situ* observation of Ti/Al and Ti/TiH₂/Al compacts upon heating

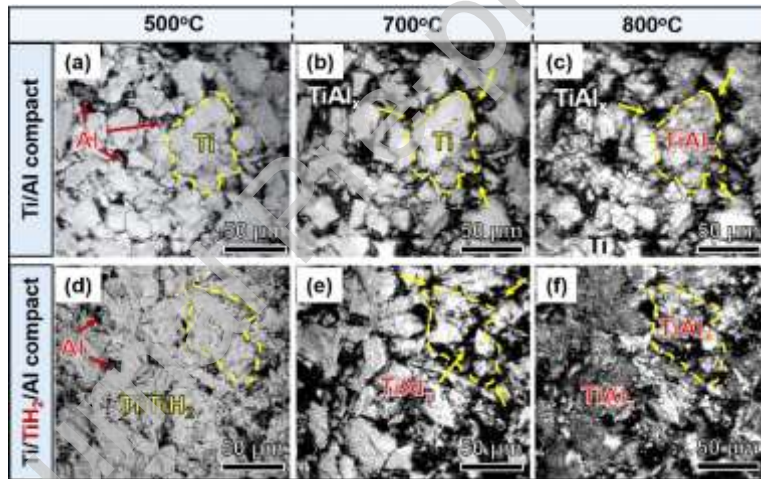


Fig. 7. Laser scanning confocal microscope (LSCM) images of the Ti/Al compact at (a) 500 °C, (b) 700 °C, and (c) 800 °C. LSCM images of the Ti/TiH₂/Al compact at (d) 500 °C, (e) 700 °C, and (f) 800 °C.

When the Ti-20Al-19Nb alloy is fabricated by powder metallurgy, the Ti and Al will react step by step upon sintering [44]. Without regard to the refractory Nb, the Ti/Al and Ti/TiH₂/Al compacts were prepared to study the effects of TiH₂ on the reaction of Ti and Al. The key reaction that determined the porosity of the sintered Ti-20Al-19Nb alloy was also figured out in this experiment.

The LSCM micrographs of the Ti/Al and Ti/TiH₂/Al compacts at 500–800 °C are shown in Fig. 7, and the videos are shown in supplementary materials S3 and S4. According to the proportion and size of the raw powders, it was judged that the dark area in the pictures corresponded to the Al powder and the bright area to the Ti powder. With the increasing temperature, the dark areas expanded in both the Ti/Al and Ti/TiH₂/Al compacts, while the prior outlines of the bright area were still distinguishable. The changes indicated that the reaction of Ti and Al proceeded in the temperature range of 500–800 °C. For the Ti/Al compact, this reaction occurred mostly in the regions of the original Al particles rather than the Ti particles. The dark areas remained separated from each other as the temperature increased, and the proportion of the dark area increased from 22.8% to 31.0% when the temperature increased from 500 °C to 700 °C (Fig. 7(a, b)). In contrast, this reaction proceeded more sufficiently in the Ti/TiH₂/Al compact. On the one hand, the dark area began to connect, surrounding the original Ti particles, and the proportion of the dark area increased from 24.6% to 40.6% when the temperature increased from 500 °C to 700 °C (Fig. 7(d, e)). On the other hand, the Ti powder was fragmented upon heating, and the average size of Ti powder particles in Ti-Al compacts decreased to 13.9 μm at 700 °C. The dark area was distributed among these fragmented Ti particles, indicating the Ti-Al intermetallic phase formed inside the original Ti particles. When the temperature increased to 800 °C, the color of most Ti particles remained bright in the Ti/Al compacts, while that of the Ti particles became dark in the Ti/TiH₂/Al compacts (Fig. 7(c, f)). The color change represented the transformation from the Ti to the TiAl_x intermetallic phase. Hence, it was assumed that the TiH₂ accelerated the reaction of Ti and Al and modified the formation mechanism of the Ti-Al intermetallic phase.

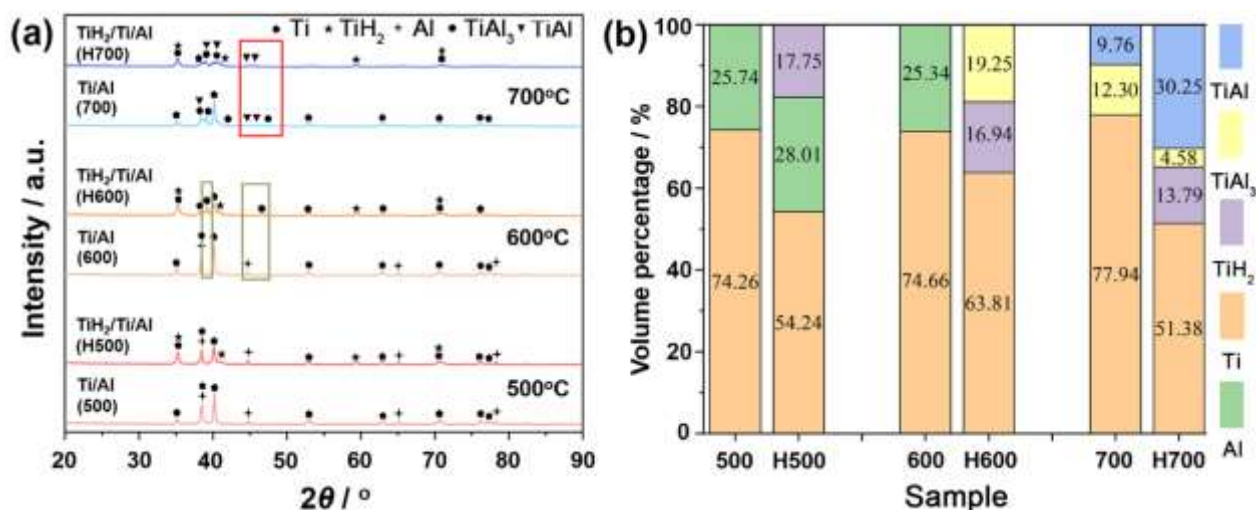


Fig. 8. (a) XRD patterns of Ti/Al and TiH₂/Ti/Al compacts quenched at 500, 600, and 700 °C. (b) Volume percentages of phases in the compacts quenched at 500, 600, and 700 °C.

To study the detailed phase transformations during the sintering process, isothermal quenching experiments were implemented on the Ti/Al and Ti/TiH₂/Al compacts at 500, 600, and 700 °C, respectively. The high-temperature phase constituent of the compacts was “frozen” to room temperature by quenching, and the XRD patterns of these compacts are shown in Fig. 8(a). At 500 °C, the α -Ti, TiH₂, and Al phases existed in their original states, and no intermetallic compounds formed in the Ti/Al and Ti/TiH₂/Al compacts. As the temperature increased, the reactions between Ti and Al proceeded, forming the intermetallic phases of TiAl₃ and γ -TiAl. Nevertheless, the formation temperatures of the two phases were different in the two systems. For the Ti/Al compact, the α -Ti and Al remained in the single element state at 600 °C, and the TiAl₃ and TiAl were simultaneously found at 700 °C, indicating that the two phases formed at 600–700 °C. In contrast, the TiAl₃ was found at a lower temperature, 600 °C, in the Ti/TiH₂/Al compact, and the Al was completely consumed at this temperature, as indicated by the frame in Fig. 8(a). Subsequently, the TiAl phase was found at 700 °C. Therefore, the TiAl₃ and TiAl were believed to form in sequence in the Ti-20Al-19Nb alloy upon sintering, and the TiH₂ predominantly promoted the

formation of TiAl_3 , which was previously speculated from the LSCM observation. The phase content was calculated from the intensity of the XRD patterns, and the results are shown in Fig. 8(b). Moreover, the SEM images of the quenched samples are shown in Fig. 9. At 600 °C, 19.25 vol.% TiAl_3 generated in the $\text{Ti/TiH}_2/\text{Al}$ compact, and the original Ti particles were surrounded by the formed TiAl_3 phase, as indicated by arrows in Fig. 9(e). The size of the Ti particles was about 5 μm , which was only one-ninth that of the raw material, indicating the fragmentation of the original Ti particles. Although no TiAl_3 phase was detected by the XRD in the Ti/Al compact quenched at 600 °C, a minor amount of this phase was found in the SEM image (Fig. 9(b)). Unlike the integral TiAl_3 cladding on the Ti particles in the compact containing TiH_2 , the TiAl_3 particles were isolated inside the original Al particles in the Ti/Al compact, accompanied by micropores nearby. Until 700 °C, the original Ti particles were surrounded by the TiAl_3 and TiAl layers in the Ti/Al compact (Fig. 9(c)), which was similar to the microstructure of the $\text{Ti/TiH}_2/\text{Al}$ compact at 600 °C (Fig. 9(e)). This phenomenon also proved that the TiH_2 accelerated the formation of TiAl_3 . In the Ti/Al compact quenched at 700 °C, the volume percentages of the TiAl_3 and TiAl phases were 12.30 vol.% and 9.76 vol.%, respectively, and the two phases formed from the outer to the inner layers of the original Ti particles. However, pores larger than 5 μm appeared in the regions of the original Al particles (Fig. 9(c)). In the $\text{Ti/TiH}_2/\text{Al}$ compact quenched at 700 °C, the original Ti particles were surrounded by three layers, which are TiAl_3 , TiAl_2 , and TiAl , from the outer to the inner, respectively. The volume percentages of the TiAl_3 and TiAl were 4.58 vol.% and 30.25 vol.%, respectively; however, the TiAl_2 failed to be detected by the XRD. The content of TiAl was larger than that of the TiAl_3 in the $\text{Ti/TiH}_2/\text{Al}$ compact at 700 °C, indicating that the reaction between Ti and Al proceeded more adequately than that in the Ti/Al compact. In addition, the size of the

formed pores was significantly reduced in the Ti/TiH₂/Al compact (Fig. 9(f)), compared with that in the Ti/Al compact. Hence, the reaction that determined the porosity of the sintered Ti-20Al-19Nb alloy might be $\text{Ti} + 3\text{Al} \rightarrow \text{TiAl}_3$, which was accelerated by the TiH₂ [45–47].

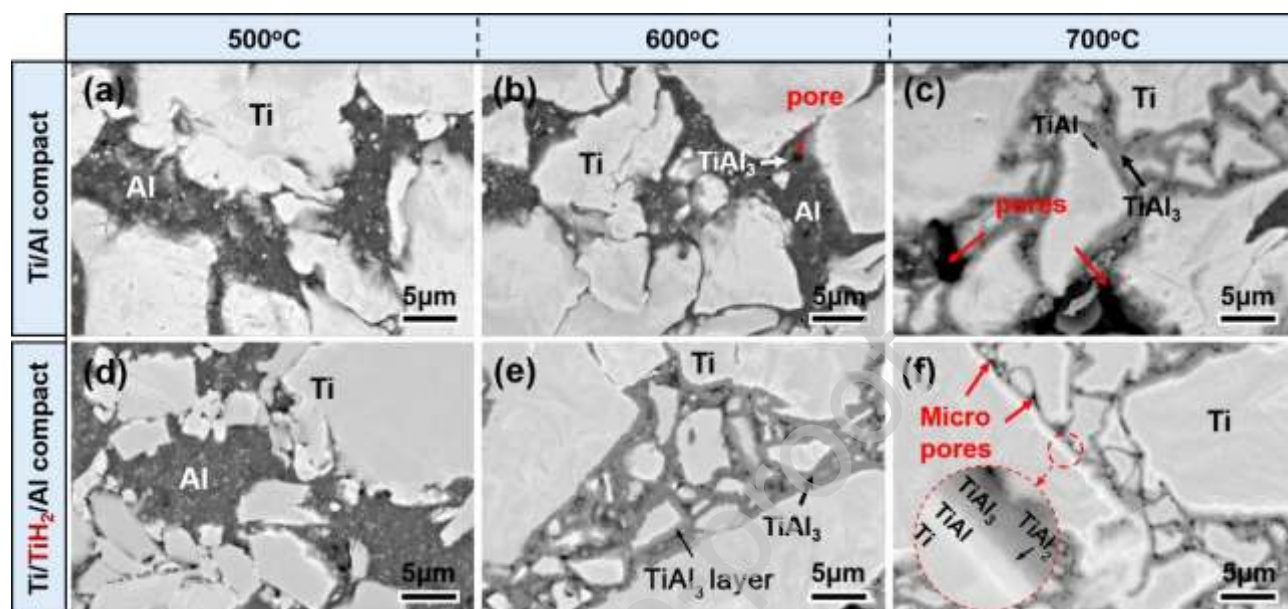


Fig. 9. BSE images of the Ti/Al compacts quenched at (a) 500 °C, (b) 600 °C, and (c) 700 °C. BSE images of the Ti/TiH₂/Al compacts quenched at (d) 500 °C, (e) 600 °C, and (f) 700 °C.

The thermodynamic and kinetic analyses were performed to interpret the underlying influential mechanism of TiH₂ on accelerating the formation of TiAl₃. In the Ti/TiH₂/Al compact, the Ti-Al reaction initiated at 500–600 °C, below which the transformation of $\alpha\text{-Ti} + \delta\text{-TiH}_2 \rightarrow \beta\text{-Ti}$ occurred (Fig. 6(b)). According to the previous studies [48–50], the diffusion rate of Al in $\beta\text{-Ti}$ was larger than that of Al in $\alpha\text{-Ti}$, as shown in Fig. 10. When the $\beta\text{-Ti}$ was generated at a lower temperature in the Ti/TiH₂/Al compact, the diffusion rate of Al was promoted. As the temperature increased, the Ti-Al intermetallic compounds formed inside the Ti particles, as well as pores along interphase boundaries, separating the Ti particles into flakes (Figs. 7(e) and 9(e, f)). The increase in the contacting area was the prerequisite for expediting the reaction. Fig. 11 shows the calculated phase diagram of the Ti-Al system and the Ti-12Al isopleth overlaid for an H composition of 44% at 1

atm, which were based on the parameters by Wang et al. [43], Qiu et al. [51], and Witusiewicz et al. [52]. When the TiH_2 and Ti were used at the ratio of 1:1 in the raw materials, the mole fraction of Ti-22Al was converted to Ti-12Al-44H. For the Ti-12Al alloy without H, the phase constituent was $\alpha + \alpha_2$ in equilibrium. For the Ti-12Al-44H alloy, the phase constituent was $\alpha_2 + \gamma + \delta\text{-TiH}_2$. Therefore, from the viewpoint of thermodynamics, the addition of TiH_2 promoted the consumption of $\alpha\text{-Ti}$ as well as the formation of the $\gamma\text{-TiAl}$ phase. Since the γ phase formed following the reaction of $\text{Ti} + 3\text{Al} \rightarrow \text{TiAl}_3 \rightarrow \text{TiAl}$, the TiH_2 might accelerate the TiAl_3 as well. In this regard, the kinetics of the reaction $\text{Ti} + 3\text{Al} \rightarrow \text{TiAl}_3$ was analyzed by one of the multi-heating rate methods, Ozawa–Flynn–Wall (O–F–W) method, which was suitable for the solid-solid reaction in the form of $\text{A} + \text{B} \rightarrow \text{C}$ [34, 35].

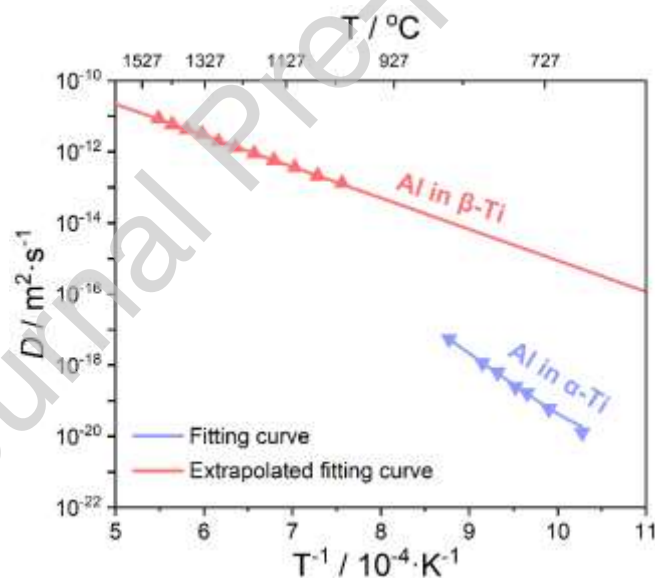


Fig. 10. Diffusion coefficient of Al in Ti based on the studies of Mishin and Herzig [48], Lee et al. [49], and Köppers et al. [50].

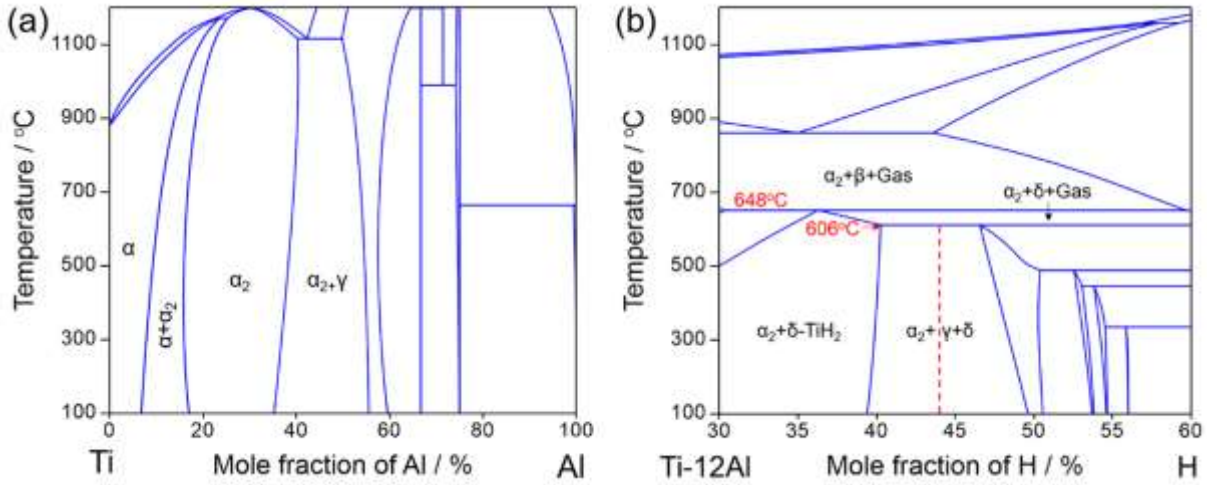


Fig. 11. (a) Binary phase diagram of Ti-Al system. (b) Ti-12Al isopleth overlaid for an H composition of 44% at 1 atm. The model's parameters are from Wang et al. [43], Qiu et al. [51], and Witusiewicz et al. [52].

The DSC curves of the Ti/Al and Ti/TiH₂/Al compacts at the heating rates of 10, 20, and 30 K min⁻¹ are shown in Fig. 12. The key reactions that affected the porosity were in the temperature range of 600–700 °C; therefore, the temperature range for the DSC curves was set as 860–970 K (587–697 °C). Since the unit of temperature in the kinetic model was Kelvin, it was used in the following kinetic analysis instead of Celsius degree. The Ti and Al might experience the reactions of $\text{Ti} + \text{Al} \rightarrow \text{TiAl}_3$, $\text{Ti} + \text{Al} \rightarrow \text{TiAl}_2$, and $\text{Ti} + \text{Al} \rightarrow \text{TiAl}$ in sequence. Only one broad exothermal peak was found on a DSC curve in this temperature range, and this peak was well fitted into three peaks by multi-peaks Gaussian fitting, as shown in Fig. 12. Among the three peaks, peak 1 was due to the thermal effect of $\text{Ti} + \text{Al} \rightarrow \text{TiAl}_3$. The peak 1 was integrated and normalized, obtaining the temperature dependence of volume fractions α , i.e., α - T curves, of the Ti/Al and Ti/TiH₂/Al compacts at different heating rates, as shown in Fig. 13.

The model of the Ozawa–Flynn–Wall method was written as Eq. (4) [34, 35, 53].

$$\log G(\alpha) = \log \left[\frac{AE}{R} \right] - 2.315 + 0.475 \frac{E}{RT} - \log \beta \quad (4)$$

where $G(\alpha)$ is the integral form of the kinetic model, A is the pre-exponential factor, E is the activation energy, R is the gas constant, T is the reaction temperature, and β is the heating rate. By replacing the $G(\alpha)$ with the expressions in Table 2 [54], the functions of α - T were obtained. For instance, the model of the AE2 mechanism is written as Eq. (5).

$$-\frac{1}{2} \log[\ln(1-\alpha)] = \log \left[\frac{AE}{R} \right] - 2.465 + 0.475 \frac{E}{RT} - \log \beta \quad (5)$$

For the AE3 mechanism, the model is written as Eq. (6).

$$-\frac{1}{3} \log[\ln(1-\alpha)] = \log \left[\frac{AE}{R} \right] - 2.294 + 0.475 \frac{E}{RT} - \log \beta \quad (6)$$

The α - T curves were fitted by using these equations, and the fitting curves are shown in Fig.

13. For the Ti/Al compact, the best fitting mechanism was Avrami-Erofeev ($n = 2$) (Eq. (5)), indicating random nucleation followed by an instantaneous growth of the nuclei. For the Ti/TiH₂/Al compact, the best fitting mechanism was Avrami-Erofeev ($n = 3$) (Eq. (6)), indicating random nucleation followed by an instantaneous growth of the nuclei as well. The reaction mechanism of Ti + Al $\rightarrow$ TiAl₃, which was interface-controlled, was hardly changed by the TiH₂ addition. However, the change of n indicated that the growth mode of TiAl₃ was different. The product grew in two-dimensional space when $n = 2$, while in three-dimensional space when $n = 3$. Therefore, in the solid-solid reaction stage of Ti and Al, granular TiAl₃ was generated inside the original Al particles for the Ti/Al compact, while the TiAl₃ layer was generated on the surface of Ti in the Ti/TiH₂/Al compact. Meanwhile, the activation energy, E , and the pre-exponential factor, A , were obtained by fitting the α - T curves. The values of E were 252 kJ mol⁻¹ and 224 kJ mol⁻¹ for the Ti/Al and Ti/TiH₂/Al compacts, respectively, and the values of A were 2.30×10^{22} and 3.05×10^{22} . Hence, the

activation energy of the reaction $\text{Ti} + \text{Al} \rightarrow \text{TiAl}_3$ decreased with TiH_2 addition, which was the underlying reason for accelerating this reaction.

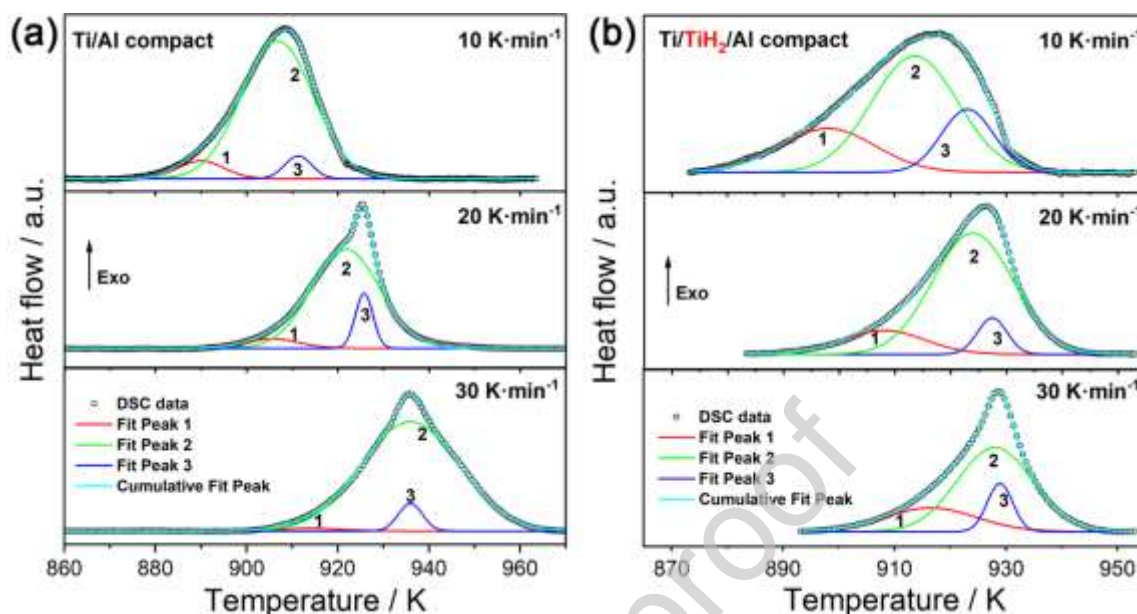


Fig. 12. DSC curves of (a) Ti/Al compacts and (b) Ti/TiH₂/Al compacts at different heating rates.

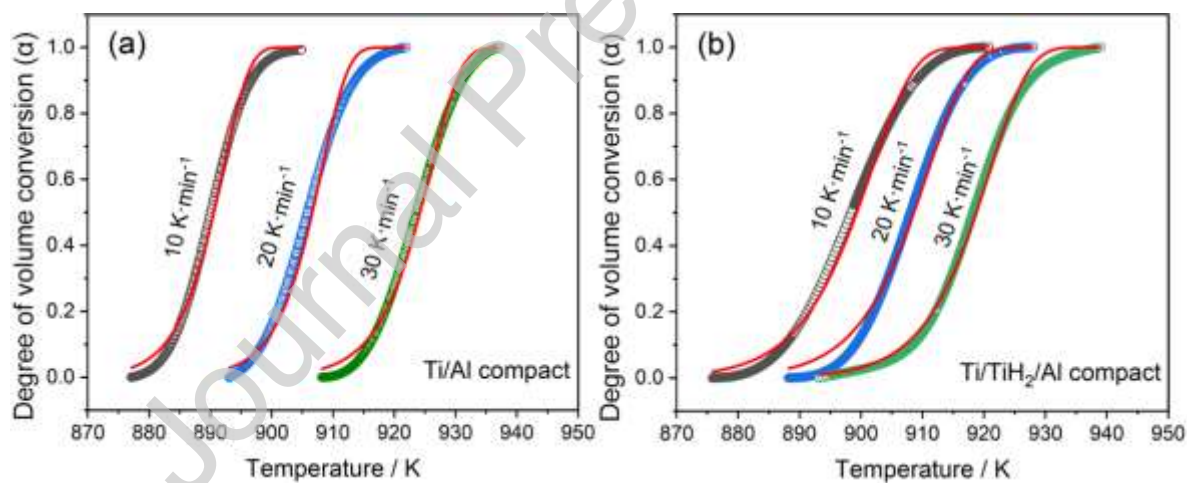


Fig. 13. Relationship between the degree of volume conversion (α) and sintering temperature for the reaction of Ti and Al determined from the DSC curves.

Table 2. Kinetic mechanisms and the corresponding integral form of the kinetic model, $G(\alpha)$ [54].

Mechanism (code)	$G(\alpha)$
Avrami-Erofeev (AE2, $n = 2$)	$2[-\ln(1 - \alpha)]^{1/2}$

Avrami-Erofeev (AE3, $n = 3$)	$3[-\ln(1 - \alpha)]^{1/3}$
Avrami-Erofeev (AE4, $n = 4$)	$4[-\ln(1 - \alpha)]^{1/4}$
Diffusion mechanism (D1)	$1/2 \cdot \alpha^2$
Diffusion mechanism (D2)	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
Diffusion mechanism (D3)	$3/2 \cdot [1 - (1 - \alpha)^{1/3}]$
Ginstling-Brounshtein (D4)	$3/2 \cdot [1 - 2\alpha/3 - (1 - \alpha)^{2/3}]$
Reaction order (R_n) $n = 1$	$-\ln(1 - \alpha)$
Reaction order (R_n) $n \neq 1$	$[1 - (1 - \alpha)^{1-n}]/(1 - n)$

3.2.3. In situ observation of Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts upon heating

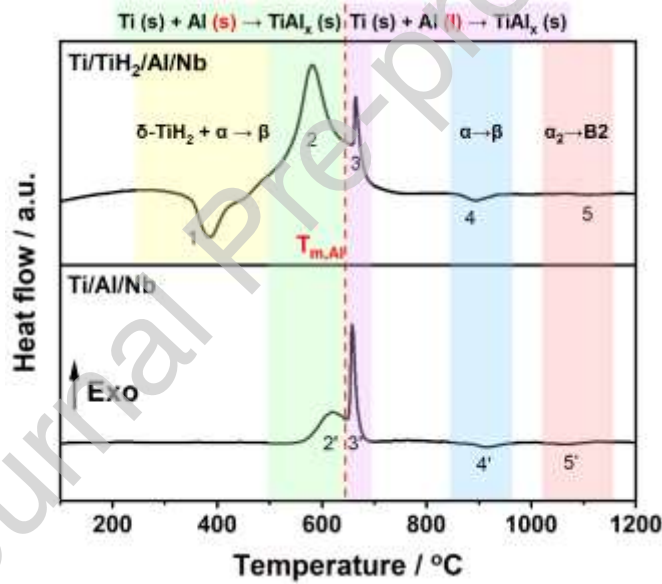


Fig. 14. DSC curves of the Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts.

To unveil the densification mechanism of the Ti-20Al-19Nb alloy by TiH₂-assisted pressureless sintering, the sintering processes of the Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts were compared. The DSC curves of the Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts upon heating are shown in Fig. 14. Below 500 °C, the endothermic peak (peak 1), which indicated the phase transformation of α -Ti + δ -TiH₂ $\rightarrow$ β -Ti, only appeared on the curve of the Ti/TiH₂/Al/Nb compact. In the temperature

range of 500–700 °C, two continuous exothermic peaks existed on both of the DSC curves. A dashed line was included in the figure to separate the two peaks, and the temperature at the position of this dashed line was the melting point of Al. Therefore, the two exothermic peaks corresponded to the reactions $\text{Ti (s)} + x\text{Al (s)} \rightarrow \text{TiAl}_x \text{ (s)}$ (peaks 2 and 2') and $\text{Ti (s)} + x\text{Al (l)} \rightarrow \text{TiAl}_x \text{ (s)}$ (peaks 3 and 3') [21], respectively. The peaks for the solid-solid reaction (peaks 2 and 2') were broad, and those for the solid-liquid reaction (peaks 3 and 3') were sharp. For the Ti/Al/Nb compact, peak 2' was lower than peak 3', indicating that Al mainly participated in the solid-liquid reaction. In contrast, peak 2 was higher than peak 3 for the Ti/TiH₂/Al/Nb compact, indicating Al mainly participated in the solid-solid reaction. Moreover, peak 2 was higher and broader than peak 2', and peak 2' initiated at a temperature 39 °C lower than peak 2. These results proved that the TiH₂ addition accelerated the solid-solid reaction of $\text{Ti (s)} + x\text{Al (s)} \rightarrow \text{TiAl}_x \text{ (s)}$, which agreed well with the *in situ* observation of the Ti/Al and Ti/TiH₂/Al compacts. According to the above studies, the sintering pores remained at the position of the transient liquid Al. In the Ti/TiH₂/Al/Nb compact, since most of the Al reacted with Ti before melting, the transient liquid Al was significantly reduced, and the resultant pores were avoided.

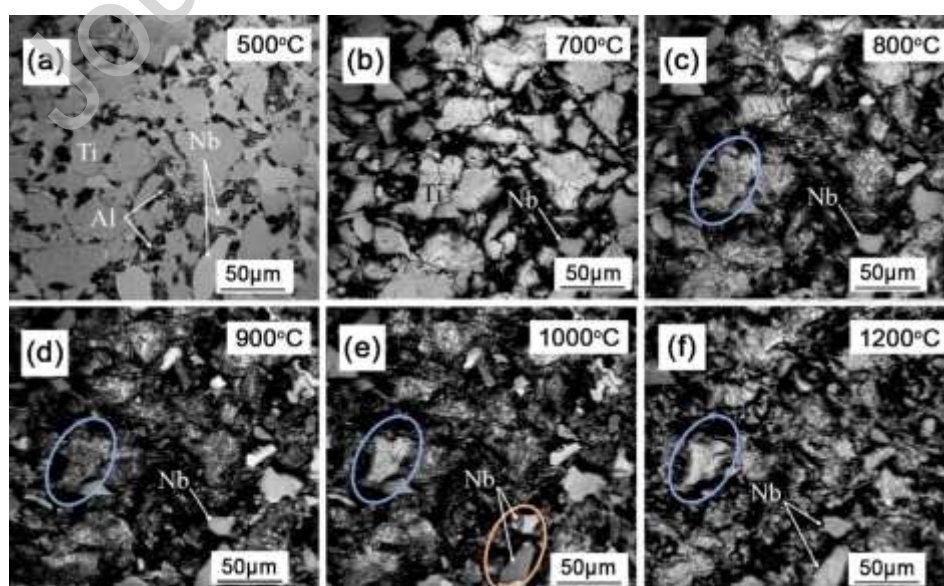


Fig. 15. LSCM images of the Ti/Al/Nb compact at (a) 500 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C, (e) 1000 °C, and (f) 1200 °C.

The LSCM micrographs of the Ti/Al/Nb at 500–1200 °C are shown in Fig. 15, and the video is shown in Supplementary Material S5. The particles, which remained unchanged as the temperature increased, were Nb, as indicated by arrows in Fig. 15. Apart from the regions of these Nb particles, the dark area in the pictures corresponded to the Al powder, and the bright area to the Ti powder. As the temperature increased, the changes in the surface morphology were divided into three stages. The first stage was at 500–700 °C. The changes in the microstructure were attributed to the reaction of $\text{Ti} + x\text{Al} \rightarrow \text{TiAl}_x (\text{s})$. In the LSCM images, the color of the original Al regions turned dark, and that of the original Ti regions remained unchanged with the increasing temperature. The area of the original Al expanded, while that of the original Ti shrank (Fig. 15(a, b)). The Nb particles hardly participated in the reaction, and this stage was the same as that for the Ti/Al compact at 500–700 °C (Fig. 7(a, b)). The second stage was at 800–900 °C. The changes in the microstructure were due to the diffusion of Ti and Al. The color of the Ti regions turned dark, and the Ti particles fragmented, as indicated by the circles (Fig. 15(c, d)). This phenomenon was similar to the fragmentation of the Ti particles in the Ti/TiH₂/Al compact at 600 °C (Fig. 9(e)), and the reason was the Al diffusion into the grain boundaries. As no TiH₂ was in the Ti/Al/Nb compact, the grain boundaries were hardly introduced by the reaction of $\alpha\text{-Ti} + \delta\text{-TiH}_2 \rightarrow \beta\text{-Ti}$. Instead, the grain boundaries formed due to the phase transformation of $\alpha\text{-Ti} \rightarrow \beta\text{-Ti}$, which corresponded to the peaks 4 and 4' at about 850 °C in Fig. 14. The α/β grain boundaries served as the diffusion paths of Al, and the formation of Ti-Al intermetallic compounds were the reason for the fragmentation of the Ti particles. Therefore, the Ti particles broke into pieces at a higher temperature of 900 °C in the Ti/Al/Nb compact, compared

with that of the Ti/TiH₂/Al compact. Apart from the Nb particles, the rest particles became uniform in color at 900 °C, indicating that the diffusion of Ti and Al became adequate. The product might be the Ti₃Al phase, which was the stable phase in equilibrium. The third stage was above 1000 °C. The changes in the microstructure originated from the diffusion of Nb. The color of the Nb particles became dark gradually, and then it returned to bright, as shown in Fig. 15(e, f), and Supplemental Material S5. Meanwhile, the color of the original Ti regions became bright due to the transformation of $\alpha_2 \rightarrow B2$, which was dependent on the diffusion of Nb [55]. This transformation corresponded to peak 5 in Fig. 14. At 1200 °C, the brightness of the surface overall tended to be uniform, indicating that the homogenization of the composition was initiated.

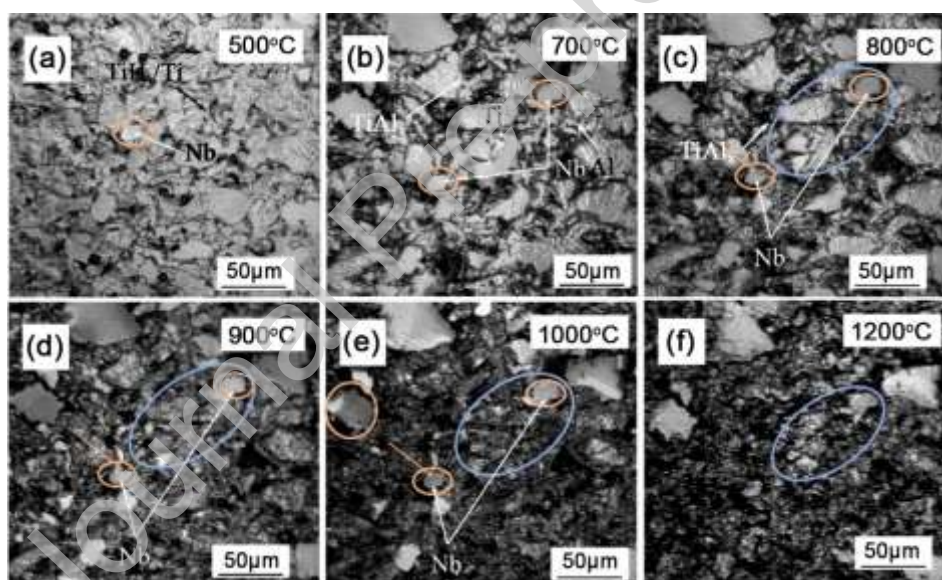


Fig. 16. LSCM images of the Ti/TiH₂/Al/Nb compact at (a) 500 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C, (e) 1000 °C, and (f) 1200 °C.

The LSCM micrographs of the Ti/TiH₂/Al/Nb at 500–1200 °C are shown in Fig. 16, and the video is shown in Supplementary Material S6. As the temperature increased, the changes in the surface morphology were also divided into three stages, and the characteristics of the three stages were analogous to those of Ti/Al/Nb compacts. The first stage was at 500–700 °C. The changes

were revealed in the regions of the Ti and Al particles (Fig. 16(a, b)). As the temperature increased to 700 °C, the color of the Al region became darker, and the area expanded, indicating the formation of the Ti-Al intermetallic phases. The color of the Ti particles remained unchanged, whereas the particles were fragmented. As mentioned above, the phase transformation of $\alpha\text{-Ti} + \delta\text{-TiH}_2 \rightarrow \beta\text{-Ti}$ induced grain boundaries in the original Ti particles, and the Al diffused into the Ti particles, forming the Ti-Al intermetallic compounds. The Ti particles were segregated by these compounds, and they existed in the form of coating layers on those refined Ti particles. The second stage was at 800–900 °C. Stripes appeared on the surface of the Ti particles, and the average size of the Ti particles reduced from 23.6 μm to 12.7 μm , indicating a large amount of Ti-Al intermetallic phases formed at 800 °C (Fig. 16(c)). Until 900 °C, the color of the Ti particles turned dark, indicating the Ti particles transformed into the Ti-Al intermetallic phases (Fig. 16(d)). In addition to the color of the Nb particles, that of the rest part became consistent, which suggested the adequate diffusion of Ti and Al. Moreover, the Nb atoms began to diffuse at this temperature, as a dark area appeared on the Nb particles, as indicated by arrows in Fig. 16(c, d). The initial temperature for the Nb diffusion was much lower than that in the Ti/Al/Nb compact. At the end of this stage, the compact began to undergo the homogenization of the composition, which was also at a lower temperature than that in the Ti/Al/Nb compact. Hence, the diffusion of Ti, Al, and Nb was accelerated by the TiH_2 addition. The third stage was above 1000 °C. The diffusion of the Nb atoms proceeded, and an expanded dark area was observed on the Nb particles (Fig. 16(e)). When the temperature reached 1200 °C, the brightness of the surface tended to be consistent, and the homogenization of the Nb element was sped up (Fig. 16(f)). Note that in the Ti/Al/Nb compact, the Ti particles remained in their original shapes above 1000 °C (Fig. 15(e, f)), since they were isolated by the sintering pores formed at 500–

700 °C. The pores were the gaps for the diffusion of Nb. In the Ti/TiH₂/Al/Nb compact, only micropores formed at 500–700 °C, and the Ti particles were still connected (Fig. 16(e, f)). The Nb atoms could diffuse among different Ti particles. Therefore, the TiH₂ promoted the uniformity of the microstructure at 1000–1200 °C.

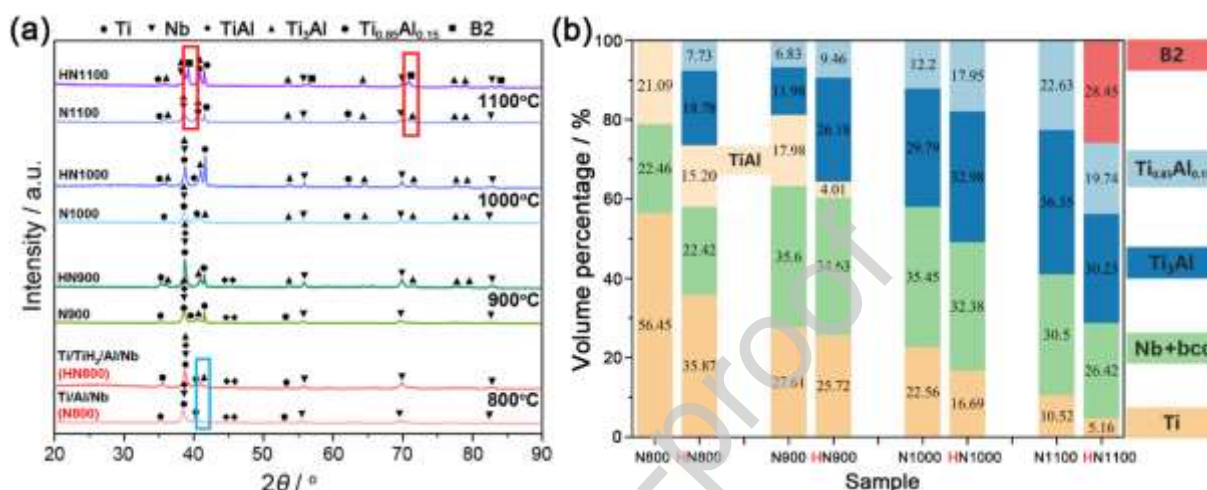


Fig. 17. (a) XRD patterns of Ti/Al/Nb and TiH₂/Ti/Al/Nb compacts quenched at 800, 900, 1000, and 1100 °C. (b) The volume percentage of phases in the compacts quenched at 800, 900, 1000, and 1100 °C.

To confirm the phase transformations during the sintering process, isothermal quenching experiments were implemented on the Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts at 500–1200 °C. The Nb hardly participated in the reactions of Ti and Al below 800 °C, and the compacts quenched at 700 °C contained TiAl₃ and TiAl phases, which were the same as those in the Ti/Al and Ti/TiH₂/Al compacts (Fig. 8(a)). The contents of the TiAl₃ and TiAl phases were higher in the Ti/TiH₂/Al/Nb compact than in the Ti/Al/Nb compact. Fig. 17 shows the XRD patterns and the phase content of the compacts at 800–1100 °C. At 800 °C, the Ti₃Al phase formed in the Ti/TiH₂/Al/Nb compact, while only the TiAl phase was found in the Ti/Al/Nb compact. The Ti₃Al was a stable phase, while the TiAl was a metastable phase in the Ti-Al and Ti-Al-H systems at this temperature (Fig. 11). It was

then believed that the addition of the TiH_2 accelerated the formation of Ti_3Al . As the temperature increased to $1000\text{ }^\circ\text{C}$, the content of the TiAl phase decreased, and that of the Ti_3Al phase increased. Moreover, the content of the Ti_3Al phase in the $\text{Ti/TiH}_2/\text{Al/Nb}$ compact was constantly higher than that in the Ti/Al/Nb compact. At $1100\text{ }^\circ\text{C}$, the B2 phase formed in the $\text{Ti/TiH}_2/\text{Al/Nb}$ compact, while only TiAl_x phases were found in the Ti/Al/Nb compact, indicating that the addition of the TiH_2 accelerated the phase transformation of $\alpha_2 \rightarrow \text{B2}$. This transformation relied significantly on the diffusion of Nb; therefore, the addition of TiH_2 accelerated the diffusion of Nb, which agreed well with the observation in Fig. 16. Since the characteristic peaks of Nb and β were hardly distinguished in the XRD patterns, the total volume percentage of Nb and β are shown in Fig. 17(b). It was also noted that a $\text{Ti}_{0.85}\text{Al}_{0.15}$ phase was identified in the XRD patterns, which was due to the diffusion of Al into the inner part of the Ti particles. The variation tendency of this phase was the same as that of the Ti_3Al phase at $800\text{--}1100\text{ }^\circ\text{C}$. The content of the $\text{Ti}_{0.85}\text{Al}_{0.15}$ phase was higher in the $\text{Ti/TiH}_2/\text{Al/Nb}$ compact than in the Ti/Al/Nb compact as well. Hence, the addition of TiH_2 facilitated the diffusion of Al.

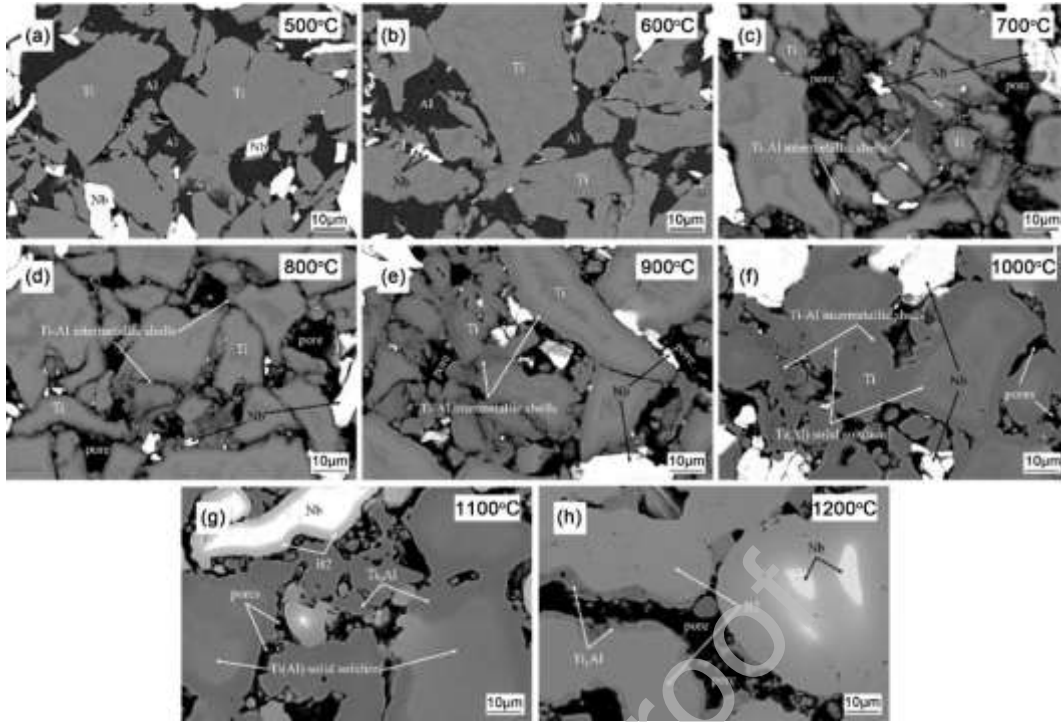


Fig. 18. BSE images of the Ti/Al/Nb compacts (a) at 25 °C, and those quenched at (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, (f) 900 °C, (g) 1000 °C, (h) 1100 °C, and (i) 1200 °C.

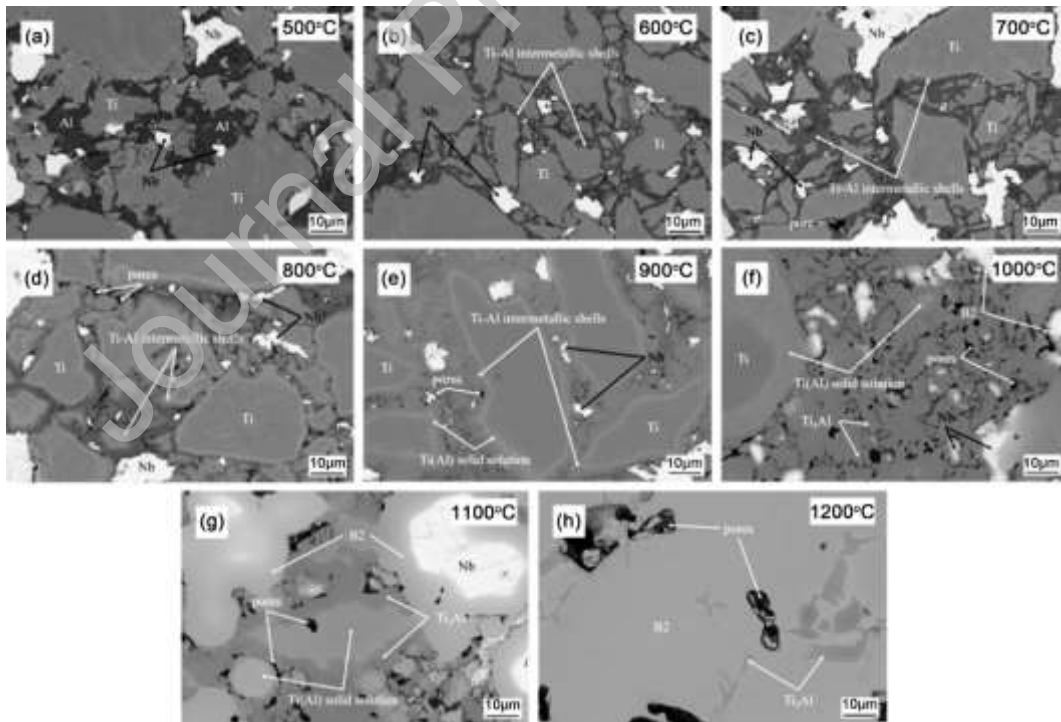


Fig. 19. BSE images of the Ti/TiH₂/Al/Nb compacts (a) at 25 °C, and those quenched at (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, (f) 900 °C, (g) 1000 °C, (h) 1100 °C, and (i) 1200 °C.

Figs. 18 and 19 show the BSE images of the Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts, respectively. At 500–700 °C, the forming temperature of the Ti-Al intermetallic layers was 600 °C for the Ti/TiH₂/Al/Nb compact, while 700 °C for the Ti/Al/Nb compact. This phenomenon was the same as that in the Ti/Al and Ti/TiH₂/Al compacts (Fig. 9). Meanwhile, the sintering pores as large as ~10 μm existed in the Ti/Al/Nb compact at 700 °C, and those of ~2 μm were found in the Ti/TiH₂/Al/Nb compact. In the Ti/Al/Nb compact, the Ti particles were isolated by the pores, and the interdiffusion between Ti and Al was decelerated. As a result, only two intermetallic layers, which were TiAl and Ti₃Al at 800 °C, formed over the entire sintering process. In contrast, five layers formed at 800 °C in the Ti/TiH₂/Al/Nb compact, and the enlarged images are shown in Fig. 20(a). Since the connective Ti particles were conducive to the diffusion of Ti and Al, a concentration gradient of Al in the Ti-Al intermetallic phases was established. According to the EDS results (Fig. 20(b)) and the element mappings (Fig. 20(c)), the intermetallic phases were TiAl₃, TiAl₂, TiAl, Ti₂Al, and Ti₃Al from the outer to the inner layer of the Ti particles. The TiAl₂ and Ti₂Al phases failed to be detected by XRD for the low content; therefore, the selected area electron diffraction (SAED) patterns were used to confirm the phases and to characterize the interfaces among the phases (Fig. 20(d–g)). In addition to the commonly accepted relationship of $(0001)[\bar{1}210]_{\text{Ti}_3\text{Al}} // (111)[01\bar{1}]_{\text{TiAl}}$ [56], the orientation relationships among the rest phases were recognized to be $(211)[0\bar{1}1]_{\text{Ti}_2\text{Al}} // (\bar{1}01)[1\bar{1}1]_{\text{TiAl}}$, $(011)[3\bar{1}1]_{\text{TiAl}} // (\bar{1}14)[1\bar{3}1]_{\text{TiAl}_2}$, and $(11\bar{2})[0\bar{1}1]_{\text{TiAl}} // (011)[\bar{1}31]_{\text{TiAl}_3}$.

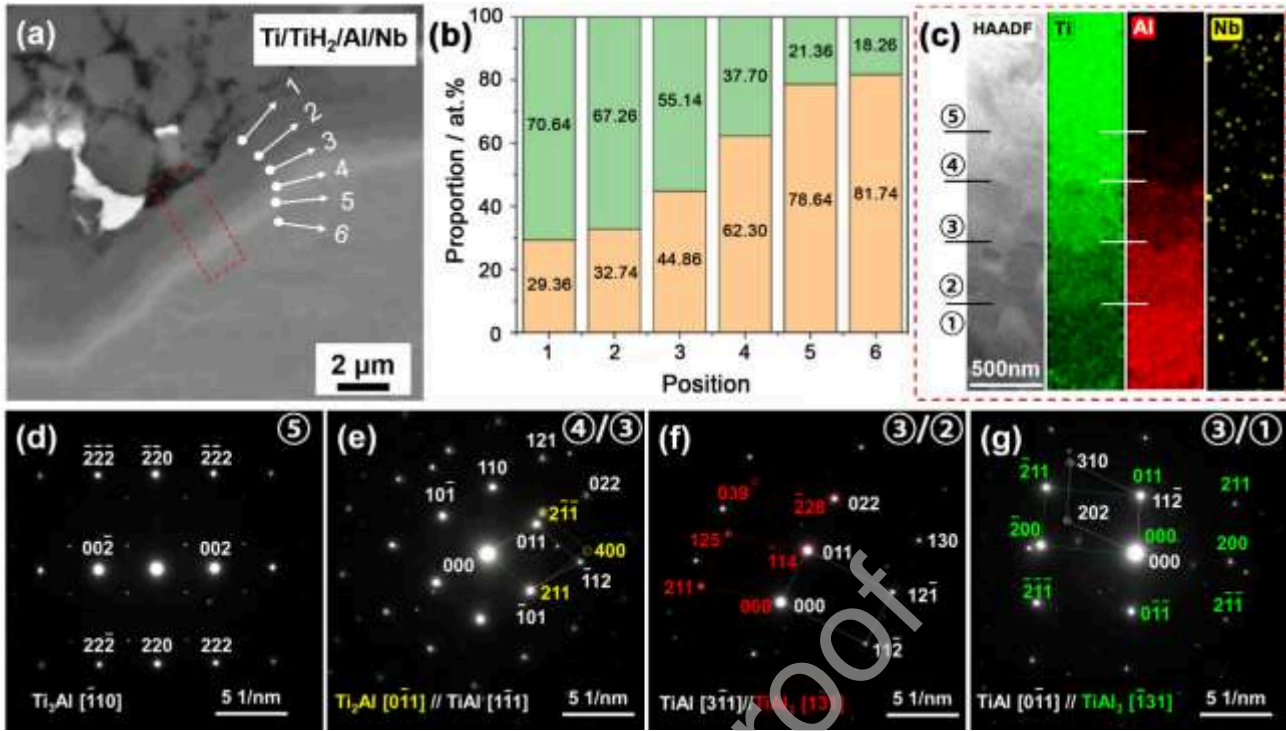


Fig. 20. (a) BSE image of the Ti/TiH₂/Al/Nb compact quenched at 800 °C. (b) EDS results corresponding to the positions in (a). (c) High-angle annular dark field (HAADF) image and element mapping. (d–g) SAED patterns of the corresponding regions in (c).

As the temperature increased, the area of the multilayers on the Ti particles expanded. At 1000 °C, the original Ti particles were composed of Ti_{0.85}Al_{0.15} solid-solution core and the Ti₃Al shell in the Ti/Al/Nb compact, since the Al was prone to diffuse in the connective Ti matrix, rather than travel across the gap to the other particles. The fragmental Ti particles transformed into the Ti₃Al phase in the Ti/TiH₂/Al/Nb compact, and the large-sized Ti particles were coated by the Ti_{0.85}Al_{0.15} layer. Meanwhile, a limited content of the B2 phase formed on the surface of the Nb particles in the Ti/TiH₂/Al/Nb compact, as indicated by arrows in Fig. 19(f). Note that pores existed in the Ti/Al/Nb compact over the entire sintering process, while in the Ti/TiH₂/Al/Nb compact, the number of the micropores abruptly increased at 1000 °C. Since the cell volume of Ti was larger than that of Ti₃Al, the formation of Ti₃Al was accompanied by the contraction of the Ti particles, which

should be responsible for these micropores. At 1100 °C, the transformation of $\alpha_2 \rightarrow$ B2 initiated in the Ti/Al/Nb compact, and the B2 phase formed on the surface of Nb particles, forming the B2-coated Nb structure (Fig. 18(g)). In the Ti/TiH₂/Al/Nb compact, the B2 layer expanded on the surface of the Nb particles, and the B2 phase formed in the center of the Ti₃Al phase. At 1200 °C, the B2 phase was surrounded by the Ti₃Al phase in the Ti/Al/Nb compact, and a small amount of Nb remained in the B2 phase. In the Ti/TiH₂/Al/Nb compact, the matrix became the B2 phase, and the equiaxed Ti₃Al phase existed inside the B2 phase. Above 1200 °C, it was the growth of the B2 phase that reduced the pores in the Ti/TiH₂/Al/Nb compact.

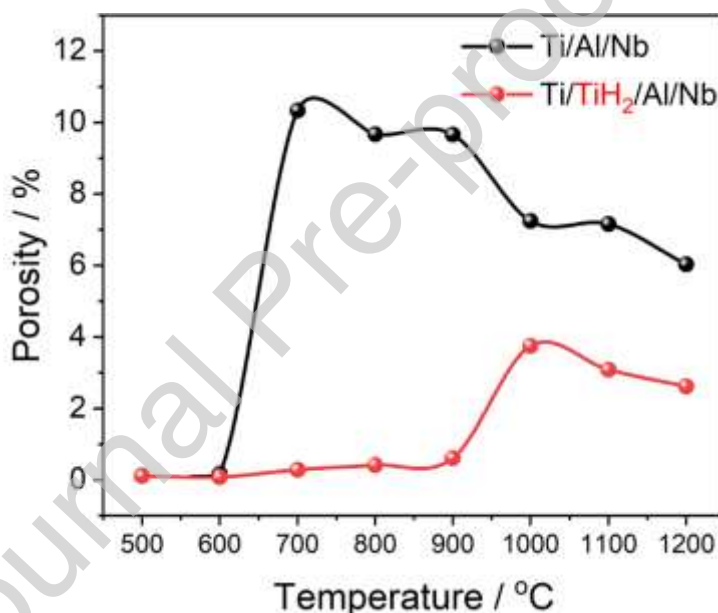


Fig. 21. Porosity of the Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts quenched at 500–1200 °C.

Based on the SEM images (Figs. 18 and 19), the porosity of the Ti/Al/Nb and Ti/TiH₂/Al/Nb compacts at 500–1200 °C was measured by the Image-Pro Plus software, as shown in Fig. 21, and the corresponding schematic diagrams for the evolution of the pores upon sintering are shown in Fig. 22. When the Ti and Al remained unreacted below 500 °C, the particles were well contacted, and few pores existed in the compact. For the Ti/Al/Nb compact, the porosity increased by 10.35% from 600 °C to 700 °C, since the rapid consumption of the liquid Al remained pores at its original

position. Most of the Al phase reacted with Ti until melting, and the reaction of $\text{Ti (s)} + \text{Al (l)} \rightarrow \text{TiAl}_x \text{ (s)}$ led to pores in the compact. The formation of these pores separated the Ti particles, which significantly decelerated the interdiffusion of Ti and Al. As the temperature increased to 900 °C, the microstructure hardly changed, and the expansion of the grains led to a slight decrease in the porosity. At 900–1000 °C, an increasing amount of Ti_3Al formed in the compact, and the Ti_3Al layer on the surface of the Ti particles grew outwards into the pores, reducing the size of the pores remarkably, as well as the porosity. With the increasing temperature, the B2 phase formed on the surface of the Nb particles, and pores formed between the Nb and the Ti_3Al particles, which was attributed to the Kirkendall effect among Ti, Al, and Nb [57, 58]. Meanwhile, the growth of the Ti_3Al phase decreased the size of the pores among the Ti_3Al phase. The overall porosity hardly changed at 1000–1100 °C. At 1200 °C, the growth of the B2 phase further decreased the porosity.

In the Ti/TiH₂/Al/Nb compact, the Ti particles broke into pieces due to the reverse eutectoid transformation, $\alpha\text{-Ti} + \delta\text{-TiH}_2 \rightarrow \beta\text{-Ti}$, at 600 °C. The formation of the TiAl_3 on the surface of the Ti fragments led to micropores at the grain boundaries, and the porosity gently increased at 600–900 °C. As the temperature increased, the Ti_3Al phase ripened, and the large Ti_3Al particles “ate” the small ones, leading to the assembling of the micropores. The porosity increased by 3.18% from 900 °C to 1000 °C. Above 1100 °C, the well-connected Ti_3Al phase provided the diffusion route of Nb, and the B2 phase formed continuously on the surface of the Nb particles and inside the Ti_3Al phase. The ripening of the B2 phase decreased the porosity of the compact. Above 1200 °C, the growth of the B2 phase decreased the porosity as well.

When the densification proceeded, the gas phase was replaced by the solid phase, and the total free energy of the system ΔG can be written as Eq. (7) [59].

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_V - 4\pi r^2 \gamma_s$$

(7)

where ΔG_V is the change in volume free energy when the gas phase is replaced by the solid phase per unit volume, r is the radius of the pores, and γ_s is the specific surface energy of the B2 particles. Under isothermal and isobaric conditions, the ΔG_V and γ_s are constant values, and the ΔG is a function of r . Since the reaction of $\text{Ti (s)} + \text{Al (s)} \rightarrow \text{TiAl}_3 \text{ (s)}$ was accelerated in the Ti-20Al-19Nb alloy by TiH_2 -assisted pressureless sintering, the large pores due to the consumption of liquid Al were reduced, and the radius of the pores decreased (Figs. 18(h) and 19(h)). Therefore, the thermodynamic origin for the densification mechanism was the decrease of the ΔG in the Ti-20Al-19Nb alloy by TiH_2 -assisted pressureless sintering. The key reaction that affected the dimension of the primary pores in the compacts is $\text{Ti (s)} + \text{Al (s)} \rightarrow \text{TiAl}_3 \text{ (s)}$. When the TiH_2 was added, the distortion of the Ti particles provided an increasing number of nucleation sites for the TiAl_3 phase (Fig. 5(e)), and the TiAl_3 formed inside the Ti/ TiH_2 particles at a lower temperature in the Ti-20Al-19Nb alloy by TiH_2 -assisted sintering. The kinetic analysis also confirmed that the activation energy of this reaction was decreased, which promoted the consumption of Al and decreased the radius of the primary pores in the compact [60, 61].

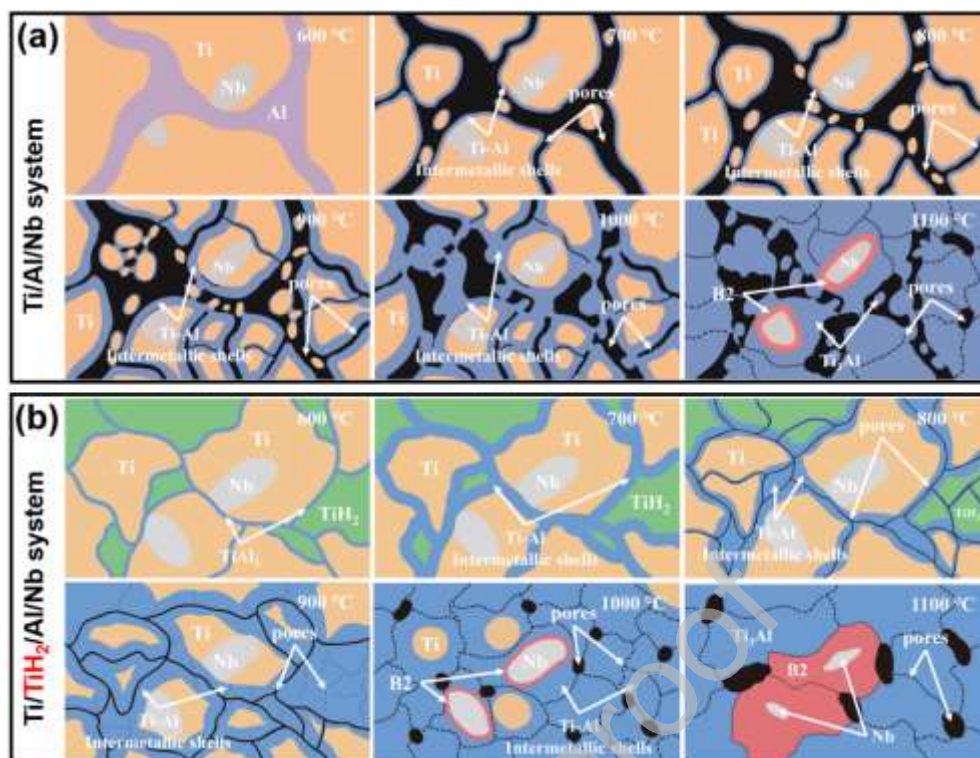


Fig. 22. Schematic diagrams of the sintering processes for (a) Ti/Al/Nb compact and (b) Ti/TiH₂/Al/Nb compact.

4. Conclusions

A dense Ti-20Al-19Nb (at.%) alloy was prepared by TiH₂-assisted pressureless sintering, and the quasi-static and dynamic compressive strengths were improved, compared with those of the alloy prepared from pure Ti powder. The densification mechanism of the Ti-20Al-19Nb alloy by TiH₂-assisted sintering was investigated in this study. The densification was associated with the phase transformation of TiH₂, the reaction of Ti and Al, and the diffusion of Ti, Al, and Nb during the sintering process.

(1) A reverse eutectoid transformation, $\alpha\text{-Ti} + \delta\text{-TiH}_2 \rightarrow \beta\text{-Ti}$, occurred at 300–400 °C, due to the TiH₂ addition. The introduced α/β and TiH₂/ β grain boundaries provided the diffusion route for Al in Ti, and the diffusion rate of Al in Ti was accelerated due to the formation of the β -Ti.

(2) The solid-liquid reaction of $\text{Ti (s)} + \text{Al (l)} \rightarrow \text{TiAl}_3 \text{ (s)}$ was the key reason for the pores in

the Ti/Al/Nb compact. Due to the TiH_2 addition, the solid-solid reaction of $\text{Ti (s)} + \text{Al (s)} \rightarrow \text{TiAl}_3$ (s) was accelerated at 500–700 °C, reducing the transient liquid Al that led to pores. The activation energy of this reaction was decreased from 252 kJ mol^{-1} to 224 kJ mol^{-1} by the addition of TiH_2 , and the two-dimensional-space growth mode of the TiAl_3 phase changed into three-dimensional-space mode.

(3) The removal of the pores reduced the diffusion barrier, and continuous diffusion pathways were provided for Ti and Al. Ti-Al intermetallic phases formed multilayers on the surface of the Ti particles, which were TiAl_3 , TiAl_2 , TiAl , Ti_2Al , and Ti_3Al from the outer layer to the inner layer. The orientation relationships were $(211)[0\bar{1}1]_{\text{Ti}_2\text{Al}} // (\bar{1}01)[1\bar{1}1]_{\text{TiAl}}$, $(011)[3\bar{1}1]_{\text{TiAl}} // (\bar{1}14)[1\bar{3}1]_{\text{TiAl}_2}$, and $(11\bar{2})[0\bar{1}1]_{\text{TiAl}} // (011)[\bar{1}31]_{\text{TiAl}_3}$.

(4) The diffusion of Nb and the phase transformation of $\alpha_2 \rightarrow \text{B2}$ were promoted by TiH_2 addition, and the ripening time for the B2 phase was increased, which reduced the pores at the grain boundaries. The porosity of the Ti/ TiH_2 /Al/Nb compact was increasing below 1000 °C. It was the accelerated ripening of B2 that decreased the porosity of the Ti-20Al-19Nb alloy by TiH_2 -assisted pressureless sintering.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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