# Microstructure Optimization by Hydrogen Treatment of β-Titanium Alloys

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Using hydrogen as a temporary alloying element is a promising approach in order to enhance mechanical properties by means of microstructure modification. Utilizing the β-stabilizing effect of hydrogen enables to retain fine β-grains during the solution heat treatment and to establish an auspicious precipitation condition of the hardening α-phase during aging. This extrinsic hydrogen effect is considered to be beneficial to mechanical properties with respect to applications of β-titanium alloys in high-strength and fatigue-critical components. The present study introduces various Thermo-Hydrogen-Processing (THP)-routes for β-titanium alloys differing considerably in β-stability. In case of highly β-stabilized Ti 38-644, which is usually solution-annealed in the single-phase β-regime, two different hydrogen treatments were devised. The microstructure modifications associated with the 1st THP-route feature a (Ti,Zr)-hydride phase. The 2nd concept utilizes lower hydrogen concentrations in a fully recrystallized β-microstructure. The near-β-titanium alloy Ti 10-2-3 is usually solution-annealed below the β-transition temperature. By means of temporary alloying with hydrogen, close attention can be paid in order to retain a small volume fraction of primary α-phase to avoid β-grain coarsening. Alternatively, solution annealing can be performed in the single-phase β-regime provided that hydrogenation has significantly reduced the β-transition temperature, thereby keeping β-grain growth moderate and facilitating a maximum volume fraction of the strengthening α-phase during subsequent aging. The microstructure response upon THP was evaluated and consequences for monotonic and cyclic strength (fatigue limit) were determined. The results clearly show that each particular THP-step has to be adapted carefully with respect to the resulting microstructural modifications which strongly affect the mechanical properties of the respective β-titanium alloy.

***Keywords***: *Thermohydrogen Processing, Ti 38-644 (Beta-C™), Ti 10-2-3, microstructure refinement, transition temperature*

## 1. Introduction

Using hydrogen as a temporary alloying element for titanium alloys is frequently referred to as Thermo-Hydrogen-Processing (THP). THP is postulated to be a powerful method improving processability, microstructure and mechanical properties by utilizing hydrogen effects on phase composition, formation of metastable phases, kinetics of phase transformations and chemical reactions in titanium alloys. Due to the high hydrogen diffusivity in titanium alloys and enormous hydrogen solubility of the bcc β-phase impeding the formation of embrittling hydrogen-induced phases (see Figure 1), hydrogenation can be performed easily by controlled diffusion in $H_2$-containing atmospheres. Subsequently to the thermomechanical treatment applied, hydrogen can be removed by controlled vacuum annealing[1,2].

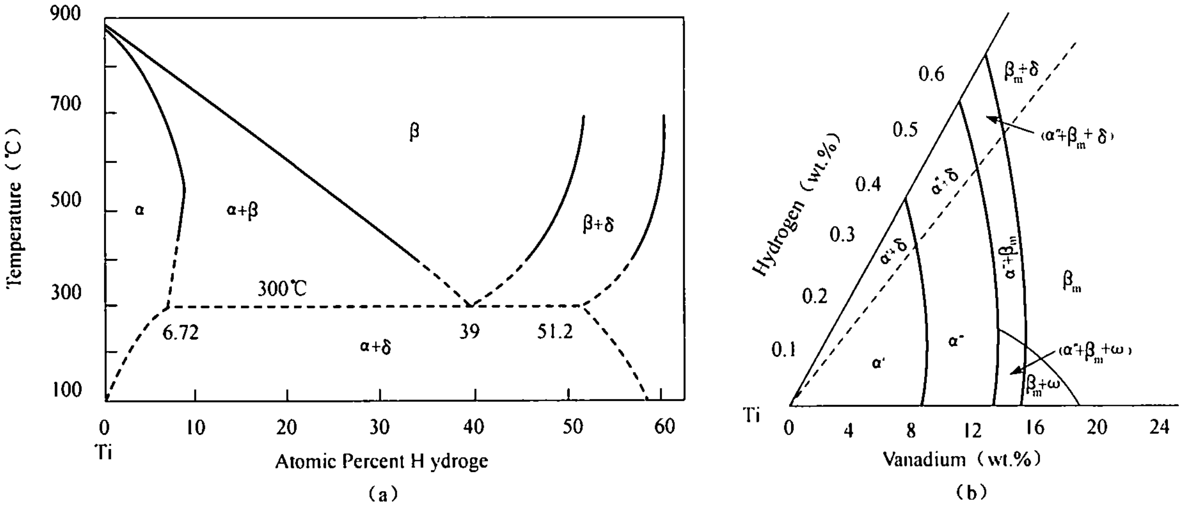


**Figure 1.** (a) The binary Ti-H phase diagram[2], (b) Metastable phase diagram for β-quenched Ti-V-H system[2]

Basic idea of THP is to utilize the de-/stabilizing effect of hydrogen on the hex α-phase/bcc β-phase. Depending on particular chemical composition of the titanium alloy (α→β) transformation or hydride formation (α→β) occurs upon hydrogenation. As shown in the Ti-H phase diagram an (α+β)-region appears and the (α+β)/β-transition temperature ($T_\beta$) decreases. The hydrogen solubility in the β-phase increases with temperature and is much higher as compared to the α-phase. The metastable phase diagram of the β-quenched Ti-V-H system shows how hydrogen affects the formation of metastable phases. An increasing hydrogen concentration reduces the critical rate of martensitic transformation and martensite start temperatures. A transformation of (hex) α′-martensite to the orthorombic α″-type and of α″ partially to the metastable β-phase (α′→

$\alpha'' \rightarrow \beta'$) occurs. The decomposition of residual β-phase ($\beta \rightarrow \beta + \beta'$) and ω-phase formation is suppressed on heating or cooling. These effects lead to a redistribution of alloying elements changing specific volumes of phases present[2].

A high volume fraction of β-phase make β-titanium alloys auspicious candidates for application of THP but in literature it is mostly addressed to ($\alpha+\beta$)-titanium alloys.

## 2. Heat Treatment of β-Titanium Alloys

In order to fully utilize the prospects facilitated by THP two metastable β-titanium alloys were studied, differing in terms of β-stability and with respect to heat treatment. Near-β high-strength Ti 10V-2Fe-3Al (Ti 10-2-3) is used for structural aerospace applications[3]. Highly β-stabilized Ti 38-644 (Beta-C™) is used in aerospace and commercial applications but also for gas and petroleum down-hole piping systems[3]. The formation of precipitatefree zones (PFZ) and continuous layers of grain boundary α-phase ($\alpha_{GB}$) are known to be the microstructural key features restricting the fatigue limit with advanced degree of hardening thereby determining the fatigue life of highly β-stabilized titanium alloys. Table I facilitates data on the chemical composition of both materials. The degree of β-stability can be specified in terms of molybdenum equivalent and transition temperature (m. e. , $T_\beta$). Ti 10-2-3 (9. 5,800℃) undergoes martensitic transformation upon quenching and forms athermal/isothermal ω-phase when annealed at approximately 300℃. β-annealing causes rapid grain coarsening and solution-annealing is performed strictly below $T_\beta$. Highly stabilized β-C (16, 780℃) usually exhibits a β-annealed microstructure. Due to the chemical composition, β-grain coarsening appears to be much more moderate[3]. The transformation of residual β ($\beta \rightarrow \beta'$) occurs upon cooling or during aging at low temperatures (e. g. 440℃).

**Table 1.** Chemical composition of β-titanium alloys studied

| | Al | V | Cr | Mo | Zr | Fe | Ti |
|---|---|---|---|---|---|---|---|
| Ti 10-2-3 | 3. 14 | 9. 78 | — | — | — | 2. 11 | bal. |
| β-C | 3. 58 | 8. 11 | 5. 39 | 4. 22 | 3. 61 | — | bal. |

Understanding microstructure/mechanical property interactions for both β-titanium alloys thoroughly was considered to be an essential requirement in order to obtain beneficial effects resulting from THP. Consequently Ti 10-2-3 and β-C were heat-treated differently and the microstructure response was studied carefully. The results served as a basis of comparison in order to evaluate microstructure modifications obtained by THP and enabled to use hydrogen as a temporary alloying element reasonably and purposeful.

According to Figure 2, Ti 10-2-3 was solution-annealed 40℃ below $T_\beta$ retaining the $\alpha_p$-phase and keeping the β-grain size constant. Subsequent aging at 525℃ led to formation of strengthening secondary β-precipitates ($\alpha_s$).

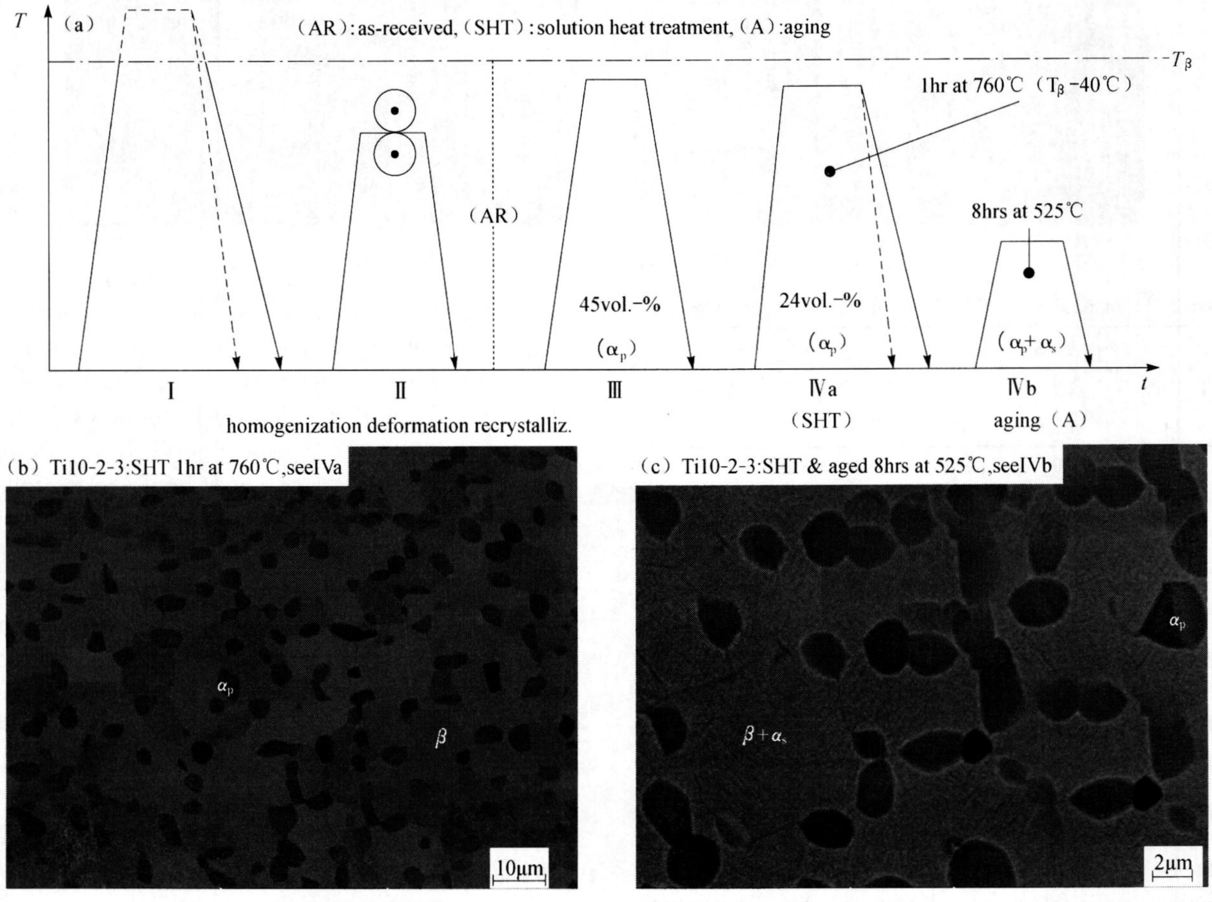


**Figure 2.** (a-c) Microstructure response of Ti 10-2-3 upon heat treatment

A typically β-annealed microstructure was received in β-C as shown in Figure 3 due to complete recrystallization above $T_\beta$. In order to avoid PFZ and formation of $\alpha_{GB}$-phase a duplex-aging cycle was applied, featuring extensive pre-aging in the temperature regime of β′-precursors leading to α-phase precipitation hardening according to $\beta \rightarrow \beta + \beta' \rightarrow \beta + \alpha$. A final aging step ultimately led to the yield strength desired. The results of mechanical tests conducted on duplex-aged β-C indicate clearly that at the expense of yield strength ($\sigma_{0.2}$) a high fatigue limit ($\sigma_f$) is attained, if a completely recrystallized β-microstructure is used as a basis for beneficial α-phase formation. Recrystallization (30min at 920℃) led to β-grain coarsening (60μm→120μm) but prospective negative effects on fatigue life were counterbalanced by a finally optimized α-phase morphology. Table 2 summarizes the mechanical properties obtained for both heat-treated β-titanium alloys. Besides $\sigma_{0.2}$ and $\sigma_f$, values for UTS, tensile ductility (el. [%]) and for the fatigue crack growth threshold ($\Delta K_{th}$[MPam$^{0.5}$]) are specified. Strength values are specified in MPa.

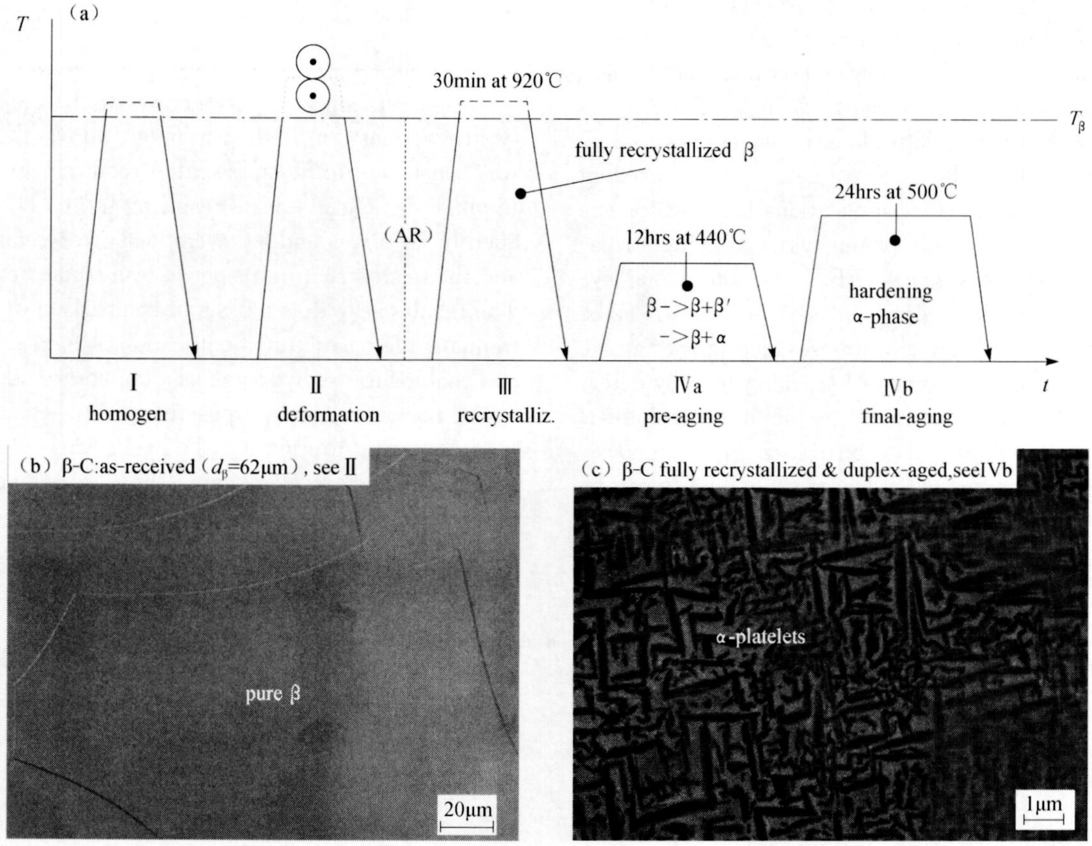


**Figure 3.** (a-c) Microstructure response of β-C upon heat treatment

**Table 2.** Mechanical properties of β-C and Ti 10-2-3 titanium alloy

| | UTS | $\sigma_{0.2}$ | el. | $\sigma_f$ | $\Delta K_{th}$ |
|---|---|---|---|---|---|
| Ti 10-2-3 | 1223 | 1162 | 7 | 675* | 2.3-3.5 |
| β-C | 1248 | 1188 | 11 | 700* | 2.9-3.3 |

* obtained under symmetrical tension-compression load ($N_f$=2×10$^6$)

## 3. Experimental

Figures 2 and 3 indicate that heat-treatment of β-titanium alloys requires the transition temperatures to be determined accurately. Consequently, THP requires reliable data on the effect of hydrogen on $T_\beta$. Since hydrogen alloying stabilizes the β-phase, $T_\beta$ is expected to decline appreciably. In order to determine $T_\beta$ accurately, hydrogenation should lead to pre-defined concentrations of hydrogen homogeneously distributed in the samples used. Therefore, hydrogen diffusion coefficients $D_H$ and hydrogen equilibrium concentrations $c_{H.equil.}$ were determined and $T_\beta$ was specified by means of metallographic methods using high-resolution (FESEM-) microscopy. Since all these experiments were conducted in the framework of THP-design for β-titanium alloys they are described briefly in the following:

*Hydrogen equilibrium solubility* $c_{H.equil.}$: Since THP is applied in a vacuum furnace with attached He-/$H_2$ gas supply facilitating (de-) hydrogenation of even semifinished products, studies on hydrogen solubility were conducted in ambient gas atmospheres ($p_{H_2}$, $T$) using thin titanium discs (∅=10mm) and $c_{H.equil.}$-values were quantified with a commerical LECO® system[4].

*Hydrogen diffusion coefficients* $D_H$: $D_H$-values were determined by evaluation of H-concentration profiles obtained after diffusion annealing of thin long rods, which were electrochemically charged before. The charging procedure was done in such a way that a Hconcentration step profile served as a starting condition[4].

*Determination of transition temperatures* $T_\beta$: In order to determine $T_\beta = f(c_H)$ samples were hydrogenated to predefined hydrogen concentrations and subsequently β-annealed for 1hr ensuring a homogeneous hydrogen distribution inside the samples used. Additional annealing for 24hrs in argon close to the expected $T_\beta$ may or may not lead to α-phase formation presumably along the β-grain boundaries. FESEM-studies were found to be most convenient in order to detect the α-phase which was finally identified by means of increased/decreased concentrations of α-stabilizing/β-stabilizing alloying elements via EDX-analyses.

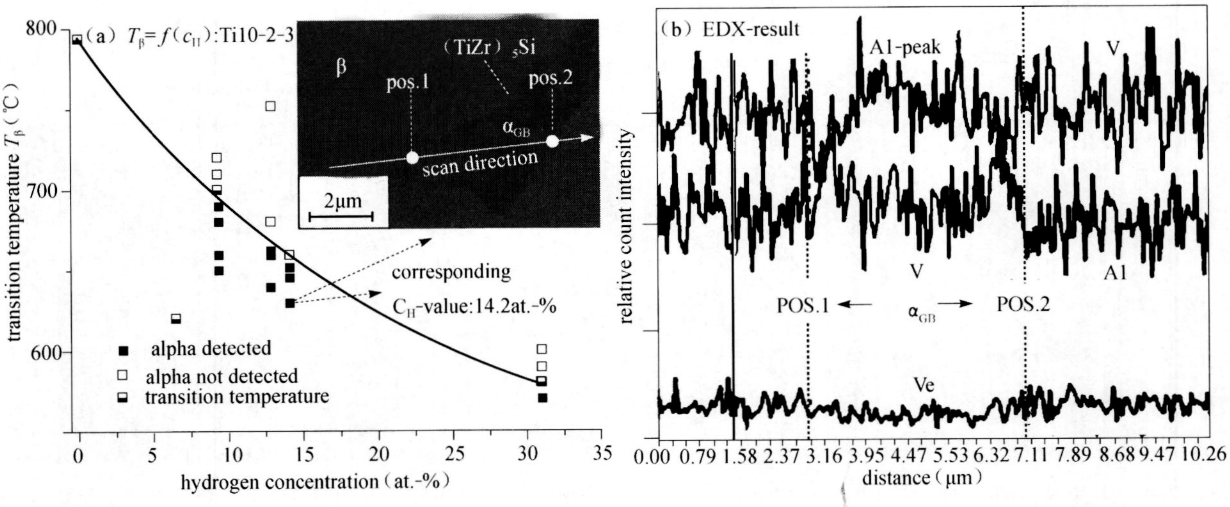


**Figure 4.** (a) Effect of hydrogen on $T_\beta$ in Ti 10-2-3, (b) α-phase evidence via EDX showing increasing Al-/decreasing V-concentration

*Hydrogen diffusion coefficients* were obtained by nummerical evaluation of electrochemically charged and diffusion-annealed samples. Additional *Matano*-studies revealed that the hydrogen concentration introduced does not affect hydrogen diffusion appreciably[4]. Accordingly, the $D_H$-values obtained can be represented in terms of activation energies $Q$ and frequency factors $D_0$ as shown in Table 3. Assuming an exclusively diffusion-controlled hydrogen uptake/release enables to calculate (de-) hydrogenation periods required to establish designated hydrogen concentrations. For example, hydrogenation at 400℃ conducted on fully aged β-C samples (∅ = 8mm) takes about 3hrs to reach the equilibrium condition. The prediction of times required for the complete (de-) hydrogenation is based on the particular $D_H$-value describing the underlying microstructure most accurately.

**Table 3.** Hydrogen diffusion coefficients $D_H$ in Ti 10-2-3 and β-C

| | as-received | | solution-treated and aged | |
|---|---|---|---|---|
| | Q[kJ/mol] | $D_0$[m²/s] | Q[kJ/mol] | $D_0$[m²/s] |
| Ti 10-2-3 | 30.85 | $3 * 10^{-7}$ | 35.6 | $6 * 10^{-7}$ |
| β-C | 21.2 | $10^{-7}$ | 35.8 | $3 * 10^{-7}$ |

## 4. Results

The determination of *hydrogen equilibrium solubilties* revealed that Ti 10-2-3 is capable to dissolve more hydrogen as compared to higher stabilized β-C at ambient $p_{H2}$ and $T$. The amount of hydrogen dissolved increased with increasing $p_{H_2}$ and decreasing hydrogenation temperature. Relating to THP the results enabled to establish designated hydrogen concentrations in both materials in order to lower the transition temperature. For example, hydrogenating near-β Ti 10-2-3 (T = 550℃, $p_{H_2}$ = 20mbar) introduces about 33at.-% hydrogen into the material and $T_\beta$ declines to about 580℃ (see Figure 4a). Accordingly, hydrogenation at 550℃ took place entirely in the (α+β)-regime, preventing β-grain coarsening.

Figure 4 shows the *β-stabilizing effect of hydrogen* in case of Ti 10-2-3 as obtained by SEM-studies. Knowing the position of $T_\beta = f(c_H)$ enables to use hydrogen as a temporary alloying element according to the specific requirements of the respective titanium alloy studied.

Using all the data obtained experimentally enabled to heat-treat both materials with close relation to $T_\beta = f(c_H)$.

In case of highly-stabilized β-C (see Figure 5) samples were fully recrystallized in order to reduce the driving force for $\alpha_{GB}$-phase formation. Optionally preaging prior to hydrogenation is intended to form β′-precursors or to facilitate an (α+β)-microstructure which was shown to be advantageous when positive catalytic effects of Pd-/PdNi-coated surfaces should be utilized[5]. Consequently, the subsequent THP exclusively aims at the refinement of strengthening α-platelets and does not facilitate a fine β-grain. In step 1 β-C is hydrogenated to various hydrogen concentrations (e. g., 9.35at.-% H significantly reducing $T_\beta$, 19.14at.-% H leading to the formation of hydrogeninduced phases, presumably ($Ti_xZr_y$)-hydrides solely along the β-grain boundaries suppressing unfavourable $\alpha_{GB}$-layers and 31.21at.-% H resulting in massive hydride formation acting as precursors for α-phase precipitation). However, the high internal stresses arising in the β-matrix from the volume expansion accompanying hydride formation can lead to surface-related crack formation[2]. In step 2 β-C is intended for aging at low temperatures (300-500℃) and for dehydrogenation by vacuum annealing (step 3). Hydrogen removal from the hydridephase facilitates the recovery of β′-or α-phase. According to Figure 5c, the THP features superfine nano-scaled α-platelets enhancing monotonic/cyclic strength.

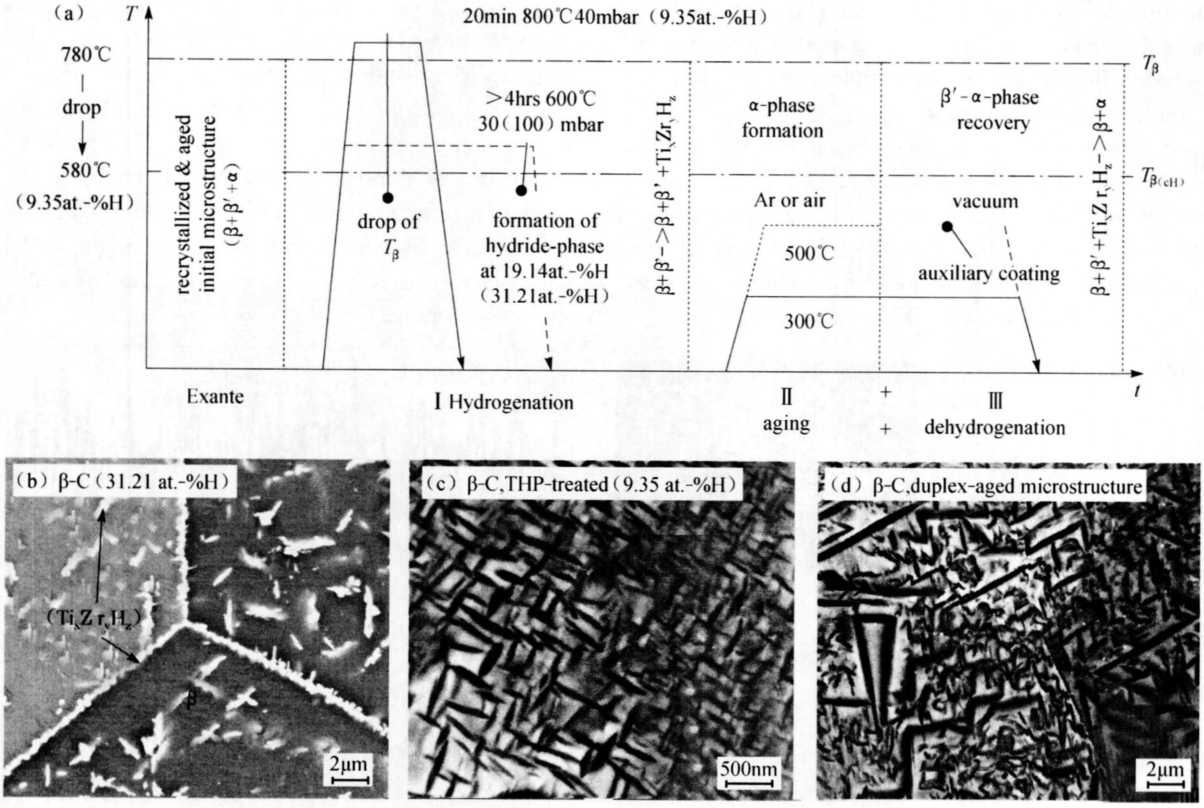
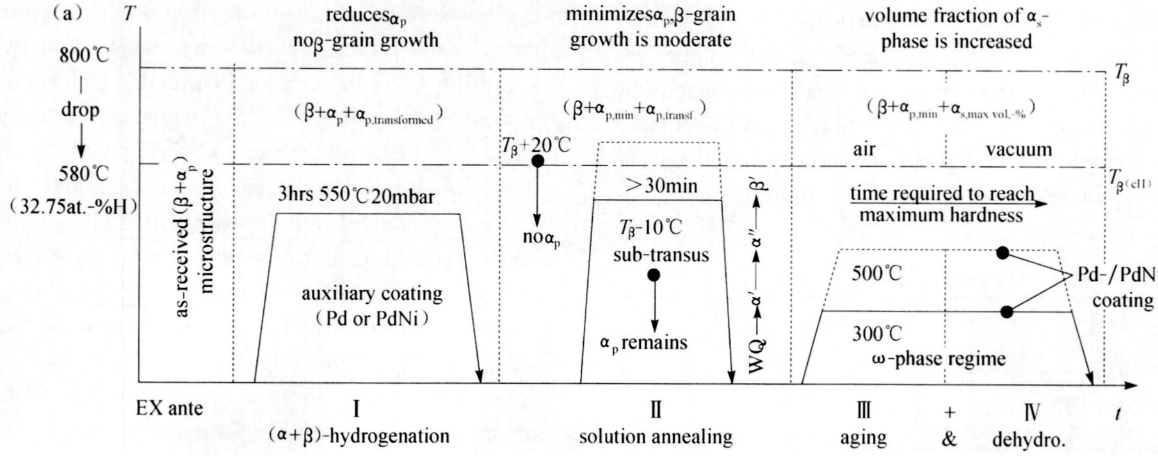


**Figure 5.** (a) THP-strategies devised for highly-stabilized β-C, (b) β-C shows massive hydride formation at 31.21at.-% H, (c) THP-treated β-C exhibits a superfine nano-sized α-phase, (d) An optimized duplex-aged microstructure serves as a reference condition in case of β-C

THP'ing of Ti 10-2-3 (see Figure 6a) goes for hydrogenating the as-received microstructure (e.g. at 550℃ 20mbar→32.75at.-% H, $T_\beta$=580℃) in the 1st step. Hydrogenation entirely in the (α+β)-regime ensures that the $\alpha_p$-phase remains, thereby keeping the β-grain size constant. Solution annealing immediately below $T_\beta$ (step 2) facilitates progressive α→β transformation preserving marginal residue of $\alpha_p$-phase keeping β-grain growth moderate. According to figures 6b and c, the $\alpha_p$-phase seems to be transformed almost completely into β-phase due to hydrogenation and solution-annealing (30min at $T_\beta$-10℃) as the EDX-studies and EBSD-measurements indicate. Ti 10-2-3 is alternatively intended to be β-annealed (dotted line), but close attention should be paid to β-grain coarsening. Both strategies facilitate an increased driving force for the strengthening $\alpha_s$-phase during the aging treatment (step 3). The THP is completed by dehydrogenation in the 4th step. Hydrogen release is accelerated by using catalytic Pd/PdNi-coatings.



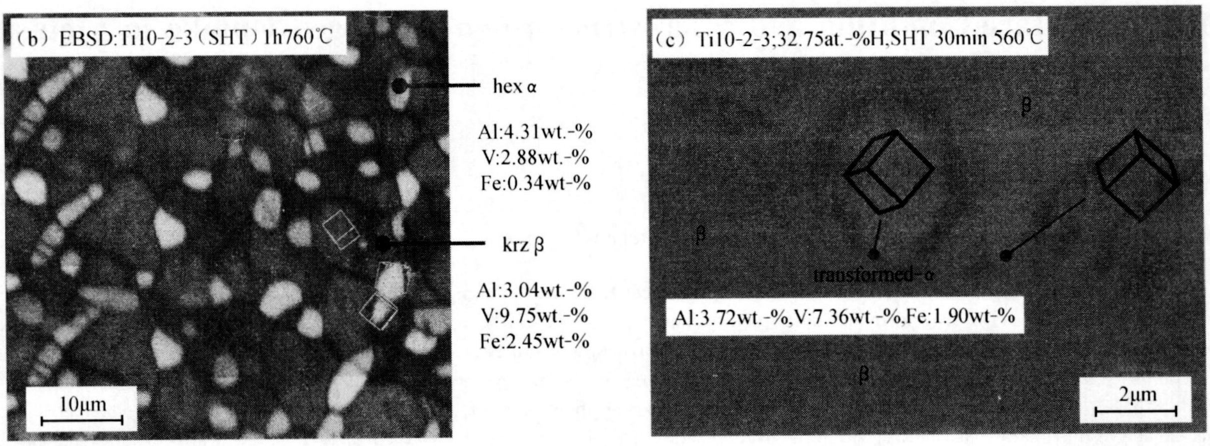


**Figure 6.** (a) Scheme of THP devised for Ti 10-2-3, (b) EBSD-result reveals hex $\alpha_p$-phase (bright) in solution-annealed Ti 10-2-3, (c) an almost complete destabilization of $\alpha_p$-phase due to 32.75at.-% H

Due to low annealing temperatures, THP of β-titanium alloys uses catalytic effects of Pd-/PdNi-coatings on (de-) hydrogenation and Zr as an auxiliary getter material[5].

## 5. Conclusions

(1) Thermohydrogen Processing (THP) seems to be a powerful and auspicious method in order to enhance mechanical properties of β-titanium alloys by means of microstructure modification. Temporary alloying with hydrogen exerts positive effects on phase composition, formation of metastable phases and phase transformation kinetics. Accurate THP requires the determination of both, metastable and stable (Ti-alloy)-$H_2$ phase diagrams.

(2) THP is considered to be most effective in case of coarse lamellar as-cast (α+β)-microstructures. The application of THP on β-titanium alloys is still rare due to the complexity of microstructures and low transition temperatures requiring (de-)/hydrogenation to be conducted at temperatures in the stability range of titanium oxide scales. Hydrogen absorption/desorption was shown to become rate-controlling in the overall (de-) hydrogenation process at lower temperatures[5]. This fact contradicts statements made by Froes *et al.*[1] concerning accurate dehydrogenation by vacuum annealing.

(3) The present study serves as an introduction into THP-design for the β-titanium alloys Ti 10-2-3 and β-C. In case of highly-stabilized β-C a 3-step strategy is devised starting out from a completely recrystallized β-microstructure which is favoured with respect to auspicious fatigue properties in terms of fatigue limit and long crack propagation. The advantages associated with a fine β-grain regarding yield strength were not taken into account. Since hydrogen suppresses the decomposition of residual β-phase, the formation of β′-precursors can be promoted by pre-aging prior to hydrogenation. Pre-aging is also considered to be essential in order to establish an appropriate surface activation when catalytic surface coatings are intended to support hydrogen absorption. Various hydrogen concentrations were introduced into β-C, which exhibits an early formation of hydrogen-induced phases, presumably ($Ti_xZr_y$)-hydrides, for $c_H$-values above approximately 15at.-% H. Consequently, the material is hydrogenated in order to a) promote α-phase formation upon hydride-precursors (19.14 and 31.21at.-% H) and b) to avoid the ($Ti_xZr_yH_z$)-phase (9.35at.-% H). Successively β-C is aged and dehydrogenated, thereby dissolving ($Ti_xZr_y$)-hydrides and facilitating the recovery of β′- and α-phase. Since hydride formation is known to be reversible and particularly occurs on β-grain boundaries in case of β-C the hydride phase is expected to be auspicious in order to prevent the $\alpha_{GB}$-phase formation during aging. Hydrogen was shown to reduce $T_\beta$ much more in β-C as compared to Ti 10-2-3.

(4) In case of the near-βtitanium alloy Ti 10-2-3 a 4-step strategy is devised aiming at high monotonic and cyclic strength. The THP utilizes hydrogenation in the (α+β)-regime preserving the $\alpha_p$-phase. Huge amounts of hydrogen can be dissolved without formation of hydrogen-induced phases significantly lowering $T_\beta$. Subsequently, the THP features solution-annealing very close (below or above) to the hydrogen-reduced transition temperature minimizing or dissolving the remaining $\alpha_p$-phase without appreciable β-grain coarsening and facilitates enhanced precipitation hardening during aging as compared to the technically heat-treated alloy. The THP is completed by hydrogen vacuum degassing.

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