Evolution of Unidirectional Solidification Microstructure and Hydrogenated Treatment of Nb-Ti-Co Quasiperitectic Alloys

Hao Wang¹, Erhu Yan¹,²*, Wei Liu¹, Chongbo Di¹, Jian Cheng¹, Renjun Huang¹, Xiaoyu Ge¹, Haoliang Chu¹, Yongjin Zou¹, Fen Xu¹, Lixian Sun¹*

¹ Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin, Guangxi, China
² State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan, China
* Corresponding Author: ¹,² Email: yeh@guet.edu.cn

Abstract. Titanium alloys have a wide range of applications, and the internal placement of hydrogen into them can modulate the microstructure of the alloys and thus have great potential for further development. However, few studies have been reported on the application of this technique to Nb-Ti-Co ternary alloys, which needs to be urgently investigated. In this paper, four types of alloys (Nb₁₀Ti₆₁Co₂₉, Nb₁₅Ti₅₅Co₃₀, Nb₂₀Ti₅₀Co₃₀, and Nb₂₅Ti₅₀Co₂₅) are selected near the eutectic point of the phase diagram to study their placement of hydrogen by both static and dynamic processes of hydrogen’s placements, focusing on the effects of the temperature, time, and hydrogen-flow rate of such processes on the amount of hydrogen placements. The relationship between the hydrogen replacement parameters and the mechanical properties of the alloys is constructed. The results show that the placed-hydrogen amount of Nb-Ti-Co as-cast alloy grows with the increase of hydrogen-flow rate and soaking (or holding) time, with an upper limit of the placed-hydrogen amount, and the pattern of the directionally-solidified alloys is similar to that of the as-cast alloys; however, at a certain soaking time and hydrogen-flow rate, although the placed hydrogen amount of both alloys rises with the increase of temperature, the placed-hydrogen amount of Nb-Ti-Co directionally-solidified alloys is always larger than that of the as-cast alloys. However, the amount of hydrogen placement in the Nb-Ti-Co directionally-solidified alloys is always larger than that in the as-cast alloys, and the amount of hydrogen placement decreases significantly as the growth rate of the alloys increases. In addition, the microhardness decreases with increasing growth rate in the directionally-solidified specimens, and the amount of hydrogen placement and microhardness increase with growing Nb content.

1. Introduction
For metals, hydrogen is usually considered as a harmful element. For example, the formation of hydrogen embrittlement [1] by a solid solution of hydrogen into the metal can weaken the properties of the metal to varying degrees. However, Kerr et al [2] in the United States found improved properties in titanium alloys by introducing moderate amounts of hydrogen, and proposed the idea of plasticization enhancement via hydrogen’s placement. Immediately after that, Senkov et al. suggested that the mechanical properties of the alloys could be improved by employing the technique of hydrogen heat treatment [3], which can be briefly summarized as: hydrogen placement → heat.
processing → hydrogen removal. Similar hydrogen treatment was performed on titanium alloys by Mamonov [4], and the tensile and fatigue properties were enhanced. Over the past decades, the hydrogen treatment process has been developed into a well-established set of techniques through intensive research by Martin, Kolachev, Ilyin and others [5-7]. In recent years, Zhang Shaoqing, Gong Bo and Zong Yingying [8-10] have conducted more systematic research on the hydrogen treatment technology of titanium alloys and derived the principles for property changes of the alloys under different hydrogen treatment processes, laying the foundation for the engineering research of hydrogen treatment.

In 2018, our team [11] reported a new system of Nb-Ti-Co hydrogen-filtering alloys among which some not only have high hydrogen permeation performance but also have good persistence performance, considered as one of the most promising hydrogen-filtering alloy films. However, the research in the field concerning the hydrogen placement of Nb-Ti-Co alloys has not been reported, and the change pattern of alloy properties before and after hydrogen’s placement is unknown. Based on this, this paper adopts the solid-state hydrogen-placement process (holding at 350°C and 450°C) to as-cast and directionally-solidified Nb-Ti-Co quasiperitectic alloys for hydrogen placement, focusing on the effects of the temperature, the time and hydrogen-flow rate of such processes on the placed-hydrogen amount of alloys, and elaborates the effects of directional-solidification growth rate and Nb (an alloy) content on the placed-hydrogen amount and mechanical properties. It also explores the feasibility of solid-state hydrogen-placement process on Nb-Ti-Co alloys on the one hand, and probes into the better performance of Nb-Ti-Co alloys on the other hand, so as to provide theoretical basis and reference for the subsequent research and application of this series of alloys.

2. Experiments
In this paper, the phase diagram of Nb-Ti-Co ternary alloys is calculated by adopting Thermo-Calc, a phase-diagram thermodynamic software, and accordingly, the element positions of the quasiperitectic alloys are explored, as shown in Figure 1 at point U₂ (Nb₈₄Ti₆₂₄Co₂₉₂). In order to facilitate the comparative study, four element points, Nb₁₀Ti₆₁Co₂₉, Nb₁₅Ti₅₅Co₃₀, Nb₂₀Ti₅₀Co₃₀ and Nb₂₅Ti₅₀Co₂₅, are preferentially selected near the U₂ quasiperitectic point for the directional-solidification experiments and hydrogen-placement experiments in this paper.

![Figure 1. Phase diagram of Nb-Ti-Co alloys in the quasiperitectic point U₂ and its four nearby element points.](image)

Nb, Ti and Co raw materials (all with 99.95 wt.% purity) are weighed based on the corresponding proportions to prepare the master alloy by melting, and then Bridgman directional-solidification experiments are performed to prepare the directional-solidification specimens. The specific experimental procedures are as follows: (i) the molten alloy solution is injected into a cylindrical mold
for cooling and molding, and an as-cast master alloy specimen of 50 mm diameter and 120 mm height is obtained; (ii) rods with diameters and heights of 3 mm and 120 mm respectively are cut around the central axis position employing wire-cutting techniques, ground and polished for later use; (iii) the rods are placed in alumina tubes with a high purity Y₂O₃ protective coating, connected to a drawbar; (iv) after being heated to 1800 K and holding for 40 min, the specimens are drawn at growth rates of 1, 3, 5, 15, 30, and 70 μm/s until they reach a length of 100 mm and then quenched rapidly in Ga-In-Sn alloy liquid to finally obtain rod-shaped directionally-solidified specimens. After the experiments, the as-cast and directionally-solidified rod specimens are cut along the longitudinal section, cleaned, ground and polished for later use, and analyzed by SEM, XRD and EDS for organizational, physical and compositional analysis.

The hydrogen placement of the four selected types of Nb-Ti-Co quasiperitectic alloys is investigated by using a test system for hydrogen placement and adopting both static and dynamic hydrogen-placement processes (denoted as Group A and Group B, respectively).

Group A: Dynamic diffusion hydrogen-placement process.
Vacuuming → the flux of argon gas → temperature rise → the flux of hydrogen gas (discharging while inputting) → heat preservation → furnace cooling to room temperature.

Group B: Static diffusion hydrogen-placement process.
Vacuuming → the flux of argon gas → the flux of hydrogen gas → temperature rise → heat preservation → furnace cooling to room temperature.

The hydrogen-placement content (wt.%) in the specimen is calculated by weighing the specimen before and after hydrogen placement.

To analyze the relationship between the placed-hydrogen amount of the alloys and the hydrogen-placement time, the hydrogen-flow rate, the hydrogen-placement temperature, growth rate and Nb content in the alloys, three sets of experiments are designed adopting the controlled variable method.

(1) Investigation of the relationship between hydrogen-placement content and hydrogen-placement time.

The dynamic process of Group A is used, with all the hydrogen-flow rates selected as 150 ml/min, and the rest of the parameters are shown in Table 1.

| $T$ (°C) | Holding time (s) |
|---------|------------------|
| 350     | 600   1500 2400 3600 5400 |
| 450     | 600   1500 2400 3600 5400 |

(2) Investigation of the relationship between hydrogen-placement content and hydrogen-flow rate.

The dynamic process flow of group A is used, with all the holding time of 3600 s. The remaining parameters are shown in Table 2.

| $T$ (°C) | Hydrogen flow (ml/min) |
|---------|------------------------|
| 350     | 50  75  100  125  150 |
| 450     | 50  75  100  125  150 |

(3) Investigation of the relationship between hydrogen-placement content and hydrogen-placement temperature.

The process of Group B is used, with the holding time of 5400 s, and the hydrogen-placement temperatures at 350°C and 450°C, which is mainly considered as the main working temperature range for Nb-Ti-Co hydrogen-separating alloy film.
Finally, the Vickers hardness of the as-cast and directionally-solidified Nb-Ti-Co quasiperitectic alloys is measured before and after the hydrogen placement, with eight points randomly selected for each specimen and averaged as the final results. The load applied in the test is 0.3 kg and the load-holding time is 15 s.

3. Results and discussions

3.1. Phase composition and microstructure of Nb-Ti-Co quasiperitectic alloys

The XRD diffraction patterns of the four clad eutectic alloys, Nb10Ti61Co29, Nb15Ti55Co30, Nb20Ti50Co30 and Nb25Ti50Co25, in the as-cast state are given in Figure 2, from which it can be seen that all the alloys are composed of three phases, namely: the BCC-(Nb, Ti) solid-solution phase, the TiCo phase, and the Ti2Co phase. The diffraction angle of 38° corresponds to the strongest diffraction peak of the BCC-(Nb, Ti) phase, implying that the content of this phase is relatively high in the alloys, while on the contrary, the content of Ti2Co phase is relatively low.

![XRD diffraction patterns of the four quasiperitectic alloys.](image)

Figure 2. XRD diffraction patterns of the four quasiperitectic alloys.

![SEM images of longitudinal sections of four Nb-Ti-Co alloys with the growth rate of 1 μm/s.](image)

Figure 3. SEM images of longitudinal sections of four Nb-Ti-Co alloys with the growth rate of 1 μm/s.
Figure 3 gives the macroscopic composition photographs of the longitudinal sections of the four alloys at a growth rate of 1 μm/s after directional solidification, from which it can be seen that each specimen contains three regions, namely, upper, middle and lower ones, corresponding to the initial transition zone, steady-state growth zone and quenching interface (solid/liquid interface) zone, respectively. The arrows in Figure 3(a) indicate the directional-solidification growth direction, and Figure 3(b)-(e) show the longitudinal cross-sectional macroscopic views of Nb10Ti61Co29, Nb15Ti55Co30, Nb20Ti50Co30, and Nb25Ti50Co25 with a growth rate of 1 μm/s, respectively. The dashed line in the bottom panel indicates the directional solidification initiation interface (the interface under the initial transition zone) and the dashed line above indicates the quenching interface, both of which are important for probing the alloy’s organizational evolution in the directional solidification.

3.2. Hydrogen placement of Nb-Ti-Co quasiperitectic alloys

3.2.1. Relationship between the time and the amount of hydrogen placement

According to the parameters in Table 1, the hydrogen pressure is 0.4 MPa and the hydrogen-flow rate is 150 ml/min. Figure 4 presents the relationship between the hydrogen-placement time and the placed-hydrogen amount for the Nb-Ti-Co directionally-solidified alloys at different growth rates. From Figure 4(a), it can be seen that the placed-hydrogen amount of alloy Nb10Ti61Co29 always increases with the extension of the holding time at 350°C, where the growth is relatively slow in 600-1500 s and relatively fast after 1500 s. Especially, the placed-hydrogen amount of the alloys rises rapidly between 1500-2400 s, and this trend slows down after 2400 s, which is more obvious at 450°C, as shown in Figure 4(b). The comprehensive analysis shows that the placed-hydrogen amount of alloy Nb10Ti61Co29 increases with the rise of hydrogen-placement time, with an upper limit of the placed-hydrogen amount at a certain temperature; the placed-hydrogen amount of the alloys is higher at 450°C, and there is still a small increase of placed-hydrogen amount after 3600 s, which implies that the upper limit of placed-hydrogen amount of the alloys is related to the temperature of hydrogen placement, and the research on this issue will be discussed below. In addition, the placed-hydrogen amount of Nb10Ti61Co29 directionally-solidified alloys is higher than that of the as-cast alloys, which is mainly because the directionally-solidified alloys have more uniform microstructure and less segregation than the as-cast alloys, which is more favorable to the diffusion of hydrogen.

![Figure 4](image-url)
Figure 5 shows the relationship between the amount and the time of hydrogen placement for the Nb-Ti-Co quasiperitectic cast alloys at 350°C and 450°C. From the figure, it can be seen that the general trend of placed-hydrogen amount for the alloys of various components rises with the increase of holding time under conditions including the hydrogen-flow rate of 150 ml/min and the temperature of 350°C (or 400°C), and the increase of the placed-hydrogen amount at each stage is similar to that of the directionally-solidified alloys in Figure 4. The increase in the placed-hydrogen amount at each stage is similar to that of the directional solidification alloys in Figure 4, where the placed-hydrogen amount in the as-cast alloys also increases relatively slowly from 600 to 1500 s and from 2400 to 3600 s, and increases rapidly from 1500 to 2400 s. For the as-cast alloys, the placed-hydrogen amount becomes progressively more with the increase of the placement time, whose upper limit also exists, and when the placement time is long enough, the increase in the placed-hydrogen amount becomes smaller and eventually reaches saturation. The four types of alloys demonstrate basically the same pattern, and the placed-hydrogen amount grows with the increase of the niobium content in the alloys of different compositions, using Nb-Ti-Co alloys for hydrogen separation, the α-Nb solid-solution phase in the alloys is the main dissolved and diffused phase of hydrogen, with the content of α-Nb solid-solution phase in the alloys positively correlated with the content of niobium in the alloys, which to some extent reveals the phenomenon that the higher the content of niobium in the alloys, the greater the placed-hydrogen amount.

In conclusion, whether it is a directionally-solidified alloy or an as-cast alloy, the placed-hydrogen amount of Nb-Ti-Co alloy rises with the increase of holding time under certain conditions, with an upper limit value. In this paper, when the hydrogen-placement time reaches 3600 s, the hydrogen-absorption process of the alloys is basically completed. In particular, it should be noted that the placed-hydrogen amounts of the directionally-solidified alloys with growth rates of 1 and 3 μm/s are much higher than those of the other alloys, possibly due to the low growth rates, which makes the internal organization of the alloys more uniform and thus can effectively increase the hydrogen-absorption amount of the very alloys.

### 3.2.2. Relationship between hydrogen-flow rate and placed-hydrogen amount

Figure 6 displays the relationship between the hydrogen-flow rate and the placed-hydrogen amount for the Nb_{10}Ti_{51}Co_{29} directionally-solidified alloys, where the hydrogen-flow rate of the as-cast alloys is used for comparison. From the figure, it can be seen that the variation of placed-hydrogen amount with hydrogen-flow rate is generally similar for the alloys at different temperatures. The general trend of the placed-hydrogen amount increases with the increase of hydrogen-flow rate, but the increase of the placed-hydrogen amount varies from one stage to another. The rise of the placed-hydrogen amount is not large at 50 ml/min, but increases when the hydrogen-flow rate reaches 75 ml/min, and then slowly decreases until 125 ml/min, until it tends to level off. In this experiment, except for the alloys with
growth rates of 1 μm/s and 3 μm/s, all other alloys have basically finished hydrogen absorption by the hydrogen-flow rate of 100 ml/min. This is consistent with the above-mentioned principles for the variation of hydrogen absorption with hydrogen-placement time.

Figure 6. Relation graph of placed-hydrogen amount and the hydrogen-flow rate for Nb_{10}Ti_{61}Co_{29} directionally-solidified alloys at different growth rates at: (a) 350°C, (b) 450°C.

Figure 7 shows the relationship between the placed-hydrogen amount and hydrogen-flow rate of the four types of Nb-Ti-Co quasi-peritectic cast alloys at 350°C and 450°C. It can be seen from the figure that the placed-hydrogen amount generally rises with the increase of hydrogen-flow rate at different temperatures, and the hydrogen absorption is basically completed at the hydrogen-flow rate of 100 ml/min. The four types of alloys present the same pattern, and the placed-hydrogen amount steps up with the increase of niobium content in the alloys of different compositions, which is consistent with the above-said results.

Figure 7. Relation graph of placed-hydrogen amount and the hydrogen-flow rate for four Nb-Ti-Co as-cast alloys at: (a) 350°C, (b) 450°C.

3.2.3. Relationship between the hydrogen-placement temperature and the placed-hydrogen amount
The influence of the hydrogen-placement temperature on the placed-hydrogen amount of Nb-Ti-Co alloys is shown in Figure 8, and it can be seen from Figure 8(a) that the placed-hydrogen amounts of both Nb_{10}Ti_{61}Co_{29} directionally-solidified and as-cast alloys rise with the increase of temperature, and the lower the growth rate of the directionally-solidified alloys, the larger the placed-hydrogen amount at the same temperature. In addition, the placed-hydrogen amount of the directionally-solidified alloys is more than that of the as-cast alloys, which is consistent with the conclusion obtained from the
previous analysis of the hydrogen-placement time factor, that is, the Nb-Ti-Co directionally-solidified alloys are more prone to hydrogen placement than the as-cast ones. Also, it can be seen from Figure 8(b) that the hydrogen-placement content increases with rising temperature for the Nb-Ti-Co alloys with different compositions. Moreover, the hydrogen absorption of the four types of alloys also rises with the increase of niobium content, which is consistent with the effect of hydrogen-placement time and hydrogen-flow rate on the placed-hydrogen amount. With the increase of temperature, the hydrogen placement of the four types of alloys demonstrates similar trends, which indicates that the effect of temperature on the amount of hydrogen replacement has a certain regularity. The diffusion of hydrogen in Nb-Ti-Co alloys usually refers to that the hydrogen jumps continuously in the interstices of crystal lattices, which is not stationary, and the jump frequency in the alloys can reach nearly $2 \times 10^{12}$ times/s at room temperature. This diffusion ability of hydrogen is obviously influenced by the temperature. As the temperature increases, the hydrogen atoms’ energy as well as their jumping ability increases, i.e., the diffusion coefficient of hydrogen increases, which leads to a rise in the placed-hydrogen amount in the alloys.

Figure 8. Relation graph between the placed-hydrogen amount and the hydrogen-placement temperature for Nb-Ti-Co alloys: (a) Nb$_{10}$Ti$_{61}$Co$_{29}$ directionally-solidified alloys, (b) Four types of as-cast alloys.

3.3. Relationship between hydrogen placement and mechanical properties of Nb-Ti-Co alloys

In this paper, the Vickers hardness of the alloys before and after the hydrogen placement is measured to reflect the effect of hydrogen placement on the mechanical properties of the alloys. Figure 9 shows the Vickers hardness of the four types of alloys in the as-cast state and at different growth rates, from which it can be seen that the hardness of both the as-cast and the directionally-solidified alloys increases to different degrees after hydrogen placement. The paper suggests that there are two main reasons for the increase in hardness: the first factor is a solid-solution strengthening effect that after the alloys absorb hydrogen, hydrogen solid solves in the lattice interstices of the α-Nb solid-solution phase of the alloys, and then causes lattice distortion as well as its solid-solution strengthening at room temperature, thus boosting the hardness of the alloys; the second is hydride precipitation strengthening, during the process of hydrogen placement, the supersaturated hydrogen will combine with the metal atoms to generate hydride precipitation diffused inside the matrix, thus achieving the effect of improving the alloys. As can be seen in Figure 10, there is a clear hydride layer on the surface of the as-cast alloys and directionally-solidified alloys after hydrogen placement. In addition, it can also be seen from Figure 9 that the hardness of all four types of alloys increased after directional solidification compared to those in the as-cast state, which indicates that directional solidification can improve the mechanical properties of the alloys by improving their organization. Recently, similar phenomena
have been reported in alloys such as NiTiAl, Ti-47Al-6Nb-0.1C and FeCoCrNiCuTi0.8 [12-14], i.e.,
the hardness of the alloys can be improved by directional-solidification techniques.

Figure 9. Hardness diagram of four types of as-cast alloys before and after hydrogen placement: (a) Nb₁₀Ti₆₁Co₂₉, (b) Nb₁₅Ti₅₅Co₃₀, (c) Nb₂₀Ti₅₀Co₃₀, (d) Nb₂₅Ti₅₀Co₂₅.

Figure 10. Images of Nb₁₀Ti₆₁Co₂₉ as-cast alloys and directionally-solidified (1 μm/s) alloys before and after hydrogen placement: (a) and (b) refers to the morphology of as-cast alloys before and after hydrogen placement, and (c) and (d) the morphology of directionally-solidified alloys before and after hydrogen placement (1 μm/s).

For the same alloy, its hardness varies at different directional-solidification growth rates, and it can be seen from Figure 9 that the alloy microhardness decreases with increasing growth rate before and after hydrogen placement, but the reasons for this are diverse. For the Nb-Ti-Co quasiperitectic alloys before hydrogen placement, although the increase in growth rate causes an increase in the content of brittle phases in the alloys compared to the content of brittle phases such as TiCo and Ti₂Co, the hardness of the alloys theoretically rises gradually, but the experimental results are contrary to this. In addition, the Nb-Ti-Co alloys are more homogeneous at low growth rates, and this homogeneity decreases as the growth rate of the alloys increases, so its mechanical properties decrease. It can be assumed that the hardness of Nb-Ti-Co alloys is determined by whether the alloys are homogeneous or not due to different growth rates rather than by the content of brittle phases. For the alloys after hydrogen placement, the hardness of the alloys decreases with the increase of the growth rate, which is
mainly related to the degree of uniformity of the alloy organization and the content of $\alpha$-Nb phase in the alloys; usually with the increase of the growth rate, the content of brittle phase in the alloys increases and the content of $\alpha$-Nb phase decreases, so the hydrogen content in the alloys drops with the increase of the growth rate after hydrogen placement. So from the overall point of view, although the effect of solid-solution strengthening and hydride formation lead to an increase in the overall hardness of the alloys, while however, the hardness of the alloys gradually decreases with the increase in the growth rate.

![Figure 11. Hardness of the four types of as-cast alloys before and after hydrogen placement: (a) before hydrogen placement, (b) after hydrogen placement.](image)

The previous study have proven that the $\alpha$-Nb phase content plays an important role in the hardness of the alloys. To further illustrate the cause of this phenomenon, the hardness of the four types of quasiperitectic alloys before and after hydrogen placement is comprehensively compared, as shown in Figure 11 in which Figure 11(a) presents the hardness comparison of the four types of alloys before hydrogen placement and Figure 11(b) presents the hardness comparison after hydrogen placement. From the Figure 11, it can be seen that the higher the Nb content in the alloys, the higher its overall hardness, both before and after hydrogen placement. Combined with the study of 3.1 in this paper, the closer the distance to the binary eutectic trench ($L \rightarrow Nb + TiCo$) and the U$_2$ quasiperitectic alloys point Nb$_{8.4}$Ti$_{62.4}$Co$_{29.2}$, the Ti$_2$Co phase content in the alloys then rises, and the $\alpha$-Nb phase content then drops; combined with Figure 1, this paper holds that the distances of the preferred four types of alloy compositions from the U$_2$ quasiperitectic alloys points are ranging from close to far as follows: Nb$_{10}$Ti$_{61}$Co$_{29}$, Nb$_{15}$Ti$_{55}$Co$_{30}$, Nb$_{20}$Ti$_{50}$Co$_{30}$ and Nb$_{25}$Ti$_{50}$Co$_{25}$, which coincides with the results in Figure 9, i.e., the alloy microhardness increases with the increase of Nb content in the alloys.

4. Conclusions

(1) The placed-hydrogen amount of Nb-Ti-Co as-cast alloys rises with the increase of hydrogen-flow rate and holding time, but after reaching certain values, the rise slows down and gradually tends to equilibrium, that is, the alloys have an upper limit of placed-hydrogen amount; at a certain holding time and hydrogen-flow rate, the placed-hydrogen amount rises with the increase of temperature, and the directionally-solidified alloys are of similar laws.

(2) The placed-hydrogen amount in Nb-Ti-Co directionally-solidified alloys is significantly larger than that in as-cast alloys, and the placed-hydrogen amount decreases as the growth rate of the alloys increases, and the placed-hydrogen amount in the alloys rises with the increase of Nb content in the alloys.

(3) The microhardness of Nb-Ti-Co alloys is significantly enhanced by hydrogen placement compared with the alloys before hydrogen production. In addition, in the directionally-solidified specimens, the microhardness decreases with increasing growth rate, and the placed-hydrogen amount of alloys and microhardness rise with increasing Nb content in the alloys.
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