

# Ultra-fine Equiaxed Grain Refinement of Titanium Alloys by Hydrogenation, Hot Working, Heat Treatment and Dehydrogenation

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## Abstract:

*This paper describes the equiaxed grain refinement and improvement of mechanical properties of titanium alloys by hydrogenation and dehydrogenation. The key point in this refinement process is the control of three different types of dislocation structure introduced by the following treatments: (1) Precipitation of hydrides and introduction of high-density dislocations into the interior and surrounding region of hydrides by aging, (2) lowering of the  $\beta$  transus temperature so that the hot-working temperature can be low enough to retain the dislocation cell structure, and (3) formation of acicular martensite and the uniform distribution of dislocations with high density in martensites by cooling from the  $\beta$  phase region. The ultra-fine grain refinement of  $\alpha + \beta$  type Ti-6Al-4V alloy can be achieved by combining the treatments (3) and (1) or (3), (2) and (1). For example, ultra-fine grains of about 1  $\mu\text{m}$  in diameter which exhibit high strength, high fatigue strength and excellent super-plastic behavior can be obtained by hydrogenation, hot rolling, quenching or aging and dehydrogenation.*

## 1. Introduction

Titanium alloys in current use are represented by  $\alpha + \beta$  alloys, and Ti-6Al-4V accounts for 90% of the  $\alpha + \beta$  titanium alloys used. Mechanical properties of the  $\alpha + \beta$  titanium alloys vary according to the microstructure. Hot working and heat treatment for grain refinement, which is effective for microstructural control, particularly for the improvement of mechanical properties, are extremely important metallurgical treatments.

Hydrogen is utilized on a trial basis as a new means of microstructural control<sup>1)</sup>. The microstructural control method is characteristic in that it involves temporary hydrogenation by adding hydrogen as alloying element, followed by hot working, heat treatment, and finally dehydrogenation. This processing sequence produces an ultrafine grain structure.

## 2. Hydrogen in titanium

Titanium and titanium alloys have a large hydrogen solubility limit and form hydrides, as can be seen from the titanium-hydrogen phase diagram<sup>2)</sup>. They can thus absorb large amounts of hydrogen. The hydrogen solubility limit of titanium is as much

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as about 2 mass% at temperatures of 500 to 600K, which is equivalent to 50 atomic percent. In other words, hydrogen atoms can exist in titanium at a rate of approximately one per titanium atom. Titanium alloys are literally packed with hydrogen atoms. Hydrogen storage alloys make ingenious use of this function. Many study reports of the past concerning the titanium-hydrogen relations deal with hydrogen storage alloys. Metallurgical phenomena that take place in hydrogen storage alloys are investigated largely from the standpoint of storing as much hydrogen as possible.

When titanium alloys and ferrous materials are used in structures, hydrogen is much detested because it embrittles them. The hydrogen content must be minimized when these materials are used as structural members. ASTM and other standards specify a maximum hydrogen content of 150 ppm. Research on hydrogen in structural materials is primarily concerned with its harmfulness and how to reduce its content<sup>3)</sup>. Many basic studies are published about the behavior of hydrogen in metals centering on its absorption and harmfulness as well<sup>4)</sup>. Concerning its utilization for the purpose of microstructural control, however, only a few published studies are available, and it is no exaggeration to say that work on this subject has just begun.

Hydrogen is a  $\beta$  stabilized element. It influences the phase transformation in expanding the  $\beta$  phase region and lowering the  $\beta$  transus temperature. The martensite phase formed by cooling from the  $\beta$  phase region is reported to be either the  $\alpha'$  phase (hcp) or  $\alpha''$  phase (orthorhombic), depending on the hydrogen content<sup>5)</sup>. Hydrogen is apt to precipitate as hydride in a relatively low temperature region of about 500 to 800K, where it is also liable to absorption. Hydrides are claimed to have crystal structures  $\delta$  (fcc) and  $\alpha$  (fct)<sup>6)</sup>. These martensite and hydride crystal structures are not considered to have any major effect on the microstructural control of the matrix described next, so they are not discussed any more here<sup>\*1)</sup>.

Continuous cooling transformation diagrams (CCT curves) are very important in controlling the microstructure of structural materials. Recently, research has been conducted on the CCT curves of hydrogenated Ti-6Al-4V<sup>7)</sup>. The authors started their work on the utilization of hydrogen for microstructural control purposes because they noticed a slight change of microstructure following dehydrogenation in the experiment which was conducted with the aim of minimizing the content of the harmful element hydrogen, and, above all, because they knew of the proposal by Amano et al.<sup>8)</sup> that the finding about the local introduction of high-density dislocations accompanying niobium hydride precipitation should be applied to the microstructural control method<sup>9)</sup>.

### 3. Ultrafine Grain Refinement by Hydrogenation—Dehydrogenation Treatment

Solute hydrogen and hydrides, particularly the latter, must be aptly used to refine the matrix structure by hydrogenation. For example, effective utilization of precipitates has become a focus of attention in recent studies on the grain refinement of the matrix in steel. Since precipitates remain unchanged in the steel, however, the grain refinement of a precipitate-free matrix

is impossible in principle. Titanium alloys that can store large amounts of hydrogen can be dehydrogenated by locally leaving a dislocation structure where a hydride is precipitated. Recrystallized grains of the same size as the hydride precipitate can thus be formed only in the matrix.

If recrystallized grains of the same size as the precipitate are to be formed, the precipitates must serve as nucleation sites for recrystallization and must be as small as possible. For  $\alpha + \beta$  titanium alloys, the most important point is in what stage of the  $\beta \rightarrow \alpha$  phase transformation to precipitate the hydride.

Concerning this point, the authors carried out their research according to the following guidelines<sup>1,10,11)</sup>. First, the  $\alpha + \beta$  titanium alloy is hydrogenated to an appropriate degree and solution treated in the  $\beta$  phase region. To provide as many sites for recrystallization nuclei as possible:

(1) The hydride is precipitated by aging at a relatively low temperature, and high-density dislocations are locally introduced and utilized as nuclei for recrystallization.

This idea was derived from the observation by Amano et al.<sup>8)</sup> of high-density dislocations introduced into the inside and outside of niobium hydrides, particularly the inside. For, the sites where high-density dislocations are piled up can become ideal sites for the formation of recrystallization nuclei on annealing. In this way, hydrides have uniquely favorable properties.

The following pretreatments are performed to provide as many sites as possible for the fine precipitation of the hydride:

(2) A dislocation cell structure is formed by hot working.  
(3) The  $\beta$  phase is divided by  $\alpha_M$  transformation, and uniform dislocations are introduced into the  $\alpha_M$  matrix.

Since the precipitation of the hydride is assumed to occur after the  $\alpha$  transformation in this case, the treatments (3) and (1) or (3), (2) and (1) are performed in combination. The former and latter treatments are collectively called the treatments A and B, respectively. Either treatment combination is followed by dehydrogenation and recrystallization annealing.

The research on the utilization of the so-called eutectic transformation in which hydride is precipitated in the course of the  $\beta \rightarrow \alpha$  transformation was initiated in the United States<sup>12)</sup>, followed by China<sup>13)</sup> and other countries. This method consists of hydrogenating Ti-6Al-4V, heating in the  $\beta$  phase region, separating the coarse  $\beta$  phase into the  $\alpha$  phase and the hydride by isothermal transformation (eutectic transformation), and refining the grain size of the resultant microstructure. This coarse-grain two-phase division method is termed the treatment C. The method can provide grain refinement, but the authors' follow-up study found that some acicular grains remained<sup>10)</sup>. The isothermal transformation temperature appears to be a key in this issue. At any rate, the optimum temperature range seems pretty narrow.

Fig. 1 schematically shows the thermal hysteresis of the three treatments A to C. If these methods are compared to steel processing methods, the former method by the present authors is equivalent to the quenching and tempering or controlled rolling method, while the latter corresponds to the austenite-pearlite (a lamellar structure of the ferrite phase and carbide) transformation method. From the point of view of grain refinement, the former method is evidently superior to the latter.

The microstructures and mechanical properties obtained when the authors applied these treatments to Ti-6Al-4V are described next<sup>1,10,11)</sup>.

\*1 Martensite and hydrides in hydrogenated titanium are said to have various crystal structures. Martensite and hydride crystal structures are generically indicated by  $\alpha_M$  and  $\delta$ , respectively.

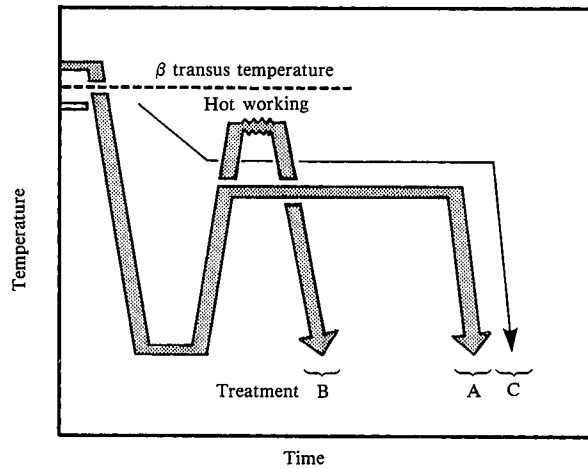


Fig. 1 Thermal hysteresis of hot working and heat treatment for hydrogenated Ti-6Al-4V alloy (treatments A to C)

**3.1 Change of  $\alpha_M$  transformation structure by hydrogenation**

When Ti-6Al-4V is hydrogenated, its  $\beta$  transus temperature drops. As a result, the  $\beta$  processing temperature can be lowered, and fine  $\beta$  phase grains can be obtained. This phenomenon can be utilized in all of the treatments A to C. The dissolution of hydrogen greatly strengthens the tendency toward the  $\alpha_M$  structure formation. When cooling is as mild as air cooling during  $\beta$  processing in the treatment A or B that makes use of this tendency, an acicular  $\alpha_M$  structure is easily formed, and many dislocations are introduced into the  $\alpha_M$  phase (see **Photo 1**). Hydrogenation in this way can divide the  $\beta$  phase and introduce uniform dislocations into the  $\alpha_M$  matrix in the preliminary  $\beta$  processing stage.

**3.2 Aging treatment (treatment A)**

To obtain a uniform ultrafine structure by the treatment A that involves aging after the  $\alpha_M$  structure formation, the material must be hydrogenated by about 1.0%. When the 1.0% hydrogenated material is aged at 700 to 800K after the  $\alpha_M$  structure formation, it is markedly hardened. When its microstructure is observed in this condition, dispersed precipitation of many hydride particles of 1  $\mu$ m or less in size is confirmed (see **Photo 2**).

The main reason for the ultrafine grain refinement is that the localized introduction of high-density dislocations by the fine dispersed precipitation of the hydride creates dislocation pileup sites, which in turn become nucleation sites in the next recrystalliza-

tion process. That is to say, if the hydride is finely precipitated, recrystallization nucleation sites can be imparted with high density<sup>1)</sup>.

Hydride precipitates are lenticular in morphology, as Amano et al.<sup>8)</sup> confirmed and advocated for niobium, and there exist high-density dislocations and midribs in their inside and outside, particularly inside. The hydride precipitation is thus considered to occur by a mechanism similar to the  $\alpha_M$  transformation or a mechanism accompanying shear deformation. This observation of dislocations inside and outside the hydride was also reported later by Koiwa et al<sup>6)</sup>. It was confirmed by dynamic observation under a transmission electron microscope that local high-density dislocation regions thus formed can serve as recrystallization nuclei in the next dehydrogenation step<sup>14)</sup>.

**3.3 Treatment involving hot working (treatment B)**

In the treatment B involving hot working, Ti-6Al-4V hydrogenated by about 0.2 to 0.5% is used for fear of cracking during hot working. A uniform ultrafine structure is obtained even with this degree of hydrogen content.

When a 0.2% hydrogenated Ti-6Al-4V material is hot rolled in the  $\alpha + \beta$  phase region after the  $\alpha_M$  structure formation, its grain size decreases with increasing rolling reduction. A 60% reduction can produce a ultrafine grain structure with a grain size of about 1  $\mu$ m (see **Photo 3**).

Hot working in the  $\alpha + \beta$  phase region forms deformation bands from dislocations from boundaries between the  $\alpha$  and  $\beta$  phases. Since the deformation bands are none other than the cell

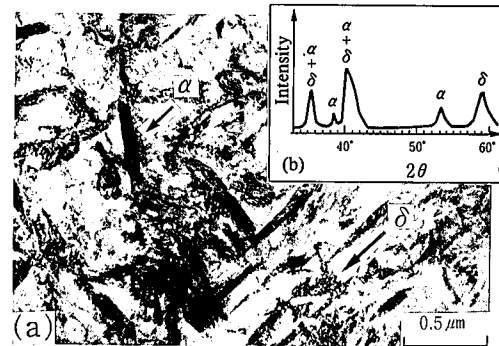


Photo 2 Transmission electron microstructure (a) and X-ray diffraction profile (b) of 1.0% hydrogenated Ti-6Al-4V alloy after treatment A ( $\alpha_M$  transformation and aging at 773K for 28.8 ks)

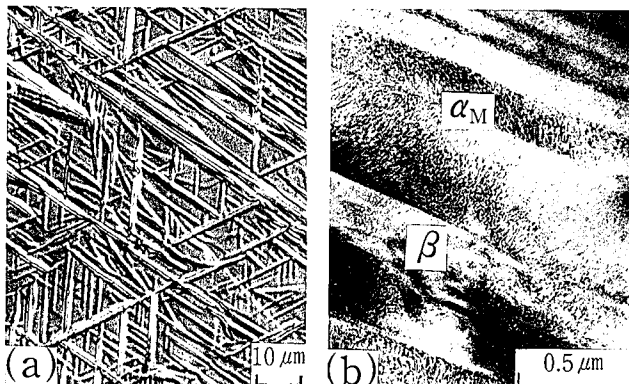


Photo 1 Optical microstructure (a) and transmission electron microstructure (b) of 1.0% hydrogenated Ti-6Al-4V alloy after  $\beta$  processing (air cooling)

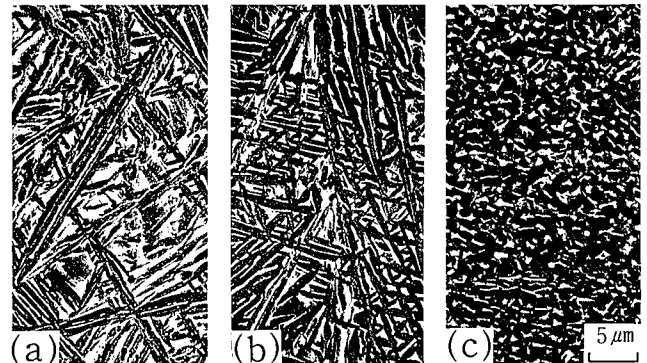


Photo 3 Scanning electron microstructures of 0.2% hydrogenated Ti-6Al-4V alloy after treatment B ( $\alpha_M$  structure formation and hot rolling in  $\alpha + \beta$  phase region at 0% (a), 20% (b), and 60% (c)) (each microstructure taken after dehydrogenation)

walls themselves<sup>15)</sup>, they operate as recrystallization nuclei. The increase in the number of cell walls or the decrease in the size of cell walls brings about the grain refinement of variants during the  $\alpha_M$  transformation on cooling after hot working and increases the number of subsequent hydride precipitation sites in the  $\alpha_M$  matrix. This may be taken as another factor responsible for the increased number of recrystallization nuclei. This is probably the reason why a small amount of oxygen (0.5% or less) suffices in the treatment B involving working, as compared with the amount of hydrogen (about 1%) required in the treatment A involving no working.

Generally, the  $\beta$  phase is lower in high-temperature deformation resistance than the  $\alpha$  phase. In a microstructure composed of both the  $\alpha$  and  $\beta$  phases, decreasing  $\beta$  phase decreases deformation resistance and remarkably improves hot workability. In other words, this method can improve hot workability as well as refine the microstructure.

**3.4 Utilization of isothermal transformation (treatment C)**

As reported by Kerr et al.<sup>12)</sup>, the 1.0% hydrogenated Ti-6Al-4V alloy is converted into the  $\beta$  phase, cooled and isothermally treated for eutectic transformation (separation into the  $\alpha$  phase and hydride), and air cooled.

**3.5 Ultrafine grain refinement by treatments A to C**

Photo 4 shows the optical microstructures of Ti-6Al-4V specimens processed by the treatment A involving aging without hot working, treatment B involving working, and treatment C involving eutectic transformation, followed by dehydrogenation annealing.

When the specimen is cooled from the  $\beta$  phase region as a preliminary step in the treatment A involving no hot working, some grain-boundary  $\alpha$  is retained, but most are fine grains (Photo 4(a)). When the specimen is cooled from the  $\alpha + \beta$  phase region, it exhibits a relatively uniform ultrafine structure without grain-boundary  $\alpha$  (Photo 4(a')). The grain size is close to about

1  $\mu\text{m}$ , or there are obtained recrystallized grains of approximately the same size as the hydride (about 1  $\mu\text{m}$  or less) precipitated during aging. When the specimen is processed by the treatment B involving hot working, it exhibits a ultra-fine and uniform structure with a grain size of about 1  $\mu\text{m}$  or less (Photo 4(b)). This is the most uniform fine-grained microstructure for the titanium alloys examined to date. When the specimen is processed by the treatment C involving eutectic transformation, it exhibits a ultra-fine structure, but acicular grains are partly retained (Photo 4(c)).

The transmission electron microstructure of a Ti-6Al-4V specimen processed by the treatment B is shown in Photo 5. It shows a uniform and equiaxed ultrafine recrystallized structure.

**4. Ultrafine Grain Refinement and improvement of Mechanical Properties by Hydrogenation**

Described below<sup>1,11)</sup> is how mechanical properties, such as tensile strength, fatigue strength, anisotropy, and superplasticity, change through successive hydrogenation, hot working and heat treatment, and dehydrogenation in that order.

**4.1 Tensile strength and fatigue strength**

Ultrafine grain refinement to about 1  $\mu\text{m}$  significantly improves the 0.2% offset yield strength and tensile strength. Fig.

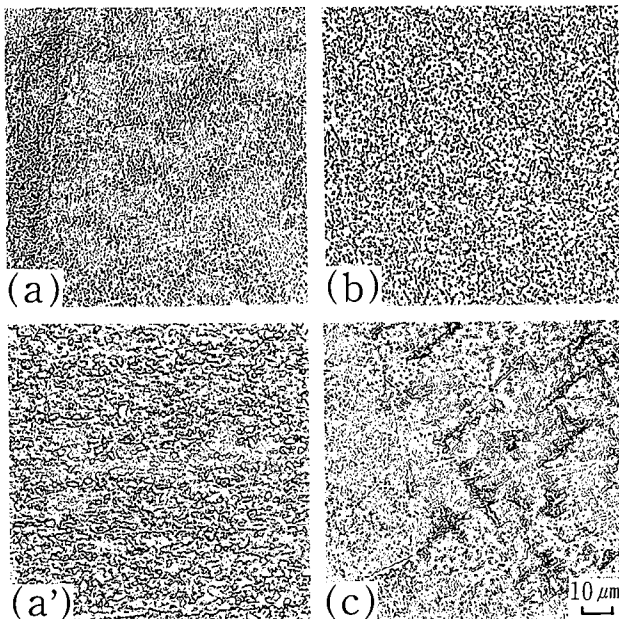


Photo 4 Optical microstructures of Ti-6Al-4V alloys after treatments A to C and dehydrogenation annealing. In treatment A, one specimen was cooled from  $\beta$  phase region (a), and another was cooled from  $\alpha + \beta$  phase region (a')



Photo 5 Transmission electron microstructure of 0.2% hydrogenated Ti-6Al-4V alloys after treatment B ( $\alpha_M$  structure formation and 60% hot rolling in  $\alpha + \beta$  phase region) and dehydrogenation annealing

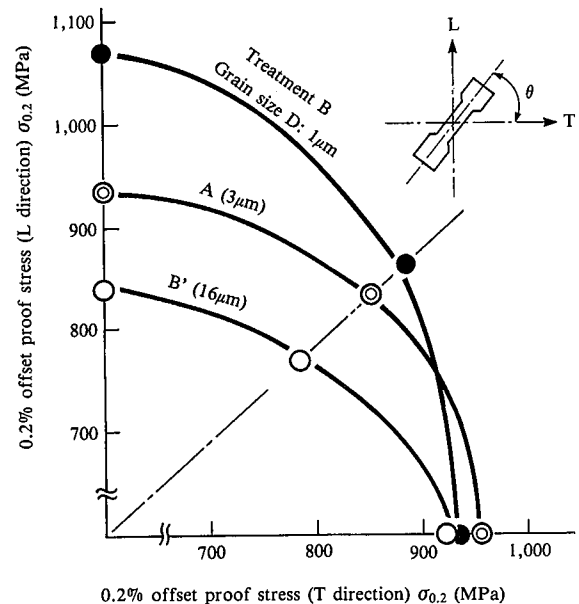


Fig. 2 Effect of ultrafine grain refinement on strength

2 shows the 0.2% offset yield strength of Ti-6Al-4V specimens processed by the treatment A, treatment B, and treatment B less hydrogenation (treatment B') in the direction (L) parallel to the rolling direction and the transverse (T) direction.

The 0.2% offset yield strength improves as a result of grain refinement by each treatment. It is to be noted, however, that a considerable degree of anisotropy results from the treatments B and B' involving hot working, but not from the treatment A involving  $\beta$  processing and aging. The latter case may be explained by texture randomizing through  $\alpha_M$  transformation by the  $\beta$  processing. It was found as a result that the treatment A is effective in increasing strength through grain refinement, while the treatment B is effective in decreasing anisotropy.

Fatigue properties improve as significantly as the 0.2% offset yield strength does (see Fig. 3). The fatigue limit of a 1- $\mu$ m

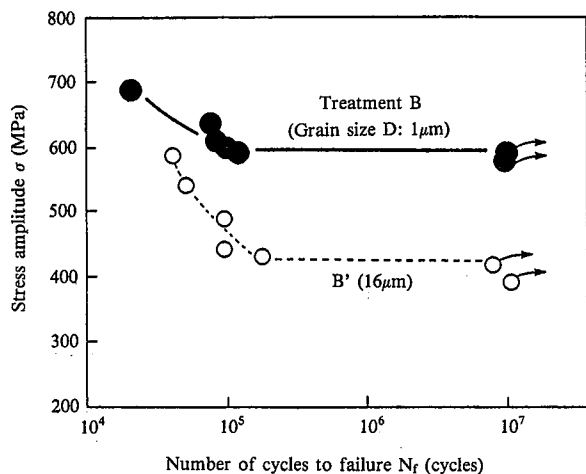


Fig. 3 Fatigue limit of ultrafine-grained Ti-6Al-4V alloy

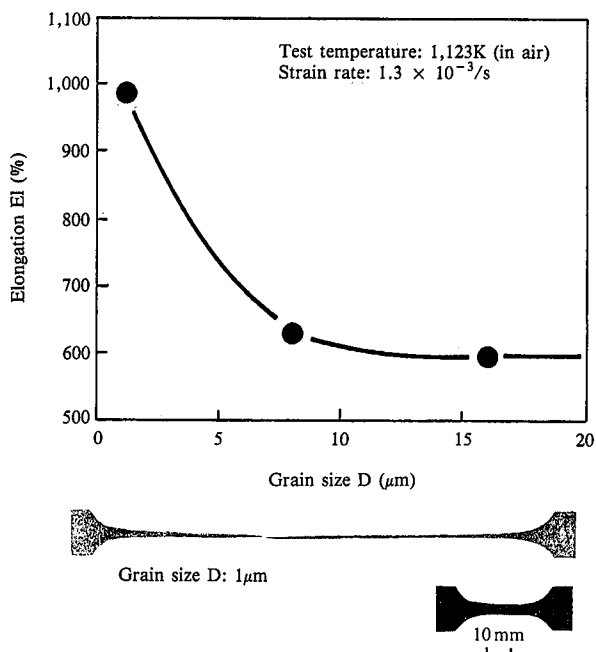


Fig. 4 Superplasticity of ultrafine-grained Ti-6Al-4V alloy

ultrafine-grained Ti-6Al-4V material is 1.5 times as high as that of a conventional Ti-6Al-4V material<sup>11</sup>.

#### 4.2 Superplasticity

Fig. 4 shows the effect of grain size on the elongation of Ti-6Al-4V specimens treated as discussed here. The 1- $\mu$ m ultrafine-grained Ti-6Al-4V material exhibits superplasticity of about 1,000%. The results of test in air are presented here. The test specimens failed rather prematurely because of surface oxidation. If tested in a nonoxidizing atmosphere, the specimens must have exhibited much greater superplasticity.

#### 5. Practical Application of Hydrogenation Technology

This technology combines  $\alpha_M$  transformation, hot working, and precipitation, through which hydrogen plays a significant role. It is interesting to note that hydrogen makes a quick exodus as soon as it finishes its assigned role. Of the many elements added to metals, there are few that act like hydrogen.

Given the characteristics discussed above, the hydrogenation technology may be applied to shaped products such as castings, forgings, rolled products, and powder metallurgy products<sup>16-19</sup>. The abilities of the technology to reduce the anisotropy of properties in products worked unidirectionally and to retain the  $\beta$  phase to a low-temperature region to allow low-temperature working should enhance the feasibility of manufacturing complex-shaped products with a minimum of oxide layer. Titanium materials processed by this technology also should benefit superplastic forming<sup>20</sup>.

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