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Continuous Cooling Transformation Characteristics of $\alpha + \beta$ Titanium Alloys

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Abstract:

The diffusional transformation structure (Widmanstätten structure) formed when $\alpha + \beta$ titanium alloys are slowly cooled from the β region was analyzed. Vanadium concentrated near the grain-boundary α phase was found to play an important role in the formation of the Widmanstätten structure. A model was proposed to describe the mechanism of the formation of Widmanstätten structure. Using the model, the phenomenon of hot ductility loss peculiar to the Widmanstätten structure was explained.

1. Introduction

When $\alpha + \beta$ titanium alloys, represented by Ti-6Al-4V, are heated, held in the β region, and cooled i.e. β-treated, they exhibit various transformed microstructures depending on the cooling rate. When the cooling rate is high, a martensitic structure or fine Widmanstätten structure (a mixture of the grain-boundary α phase and side-plate α phase) is formed. When the cooling rate is lower, a coarse Widmanstätten structure is formed. These structures excel a fine equiaxed structure in fracture toughness and creep properties[1,2]. Thus, β-treatment is greatly advantageous on an industrial basis. On the other hand, however, $\alpha + \beta$ titanium alloys close to the α type are particularly poor in hardenability. On cooling from the β region, the difference of cooling rate between the surface and center of the specimen produces a microstructural heterogeneity, hence uneven mechanical properties[1,3].

For applications where tensile strength, ductility and fatigue strength are required, titanium alloys with a fine equiaxed structure converted form the coarse Widmanstätten structure by heavy working and annealing in the $\alpha + \beta$ region are used. The coarse Widmanstätten structure is markedly poor in hot workability in the $\alpha + \beta$ region. To improve hot workability, study must be made into the mechanism whereby the Widmanstätten structure is formed.

From the above point of view, the author and his coworker studied the effect of the cooling rate on the microstructural formation of β-treated titanium alloys by systematically changing the cooling rate from the β region[4], and constructed continuous cooling transformation diagrams[5]. Particularly in Reference 4), they discussed transformed structures and hardness changes from the standpoint that shear and diffusional components of transformation compete with each other. They made a detailed study of the mechanism whereby the transformed structure is formed in the relatively high cooling rate region where the two components compete, and reported the results of the study.

This article presents the results of another study conducted on the mechanism of formation of the transformed structure in the cooling rate region where the diffusional transformation component is predominant.

2. Experimental Methods

The experimental materials are Ti-6Al-4V (with the β transus of 990°C) and Ti-6Al-6V-2Sn (with the β transus of 935°C), both double vacuum arc remelted. Their compositions are given in **Table 1**. Ti-6Al-4V and Ti-6Al-6V-2Sn were finally rolled in the $\alpha + \beta$ region into a 20-mm square bar and 12-mm thick plate, respectively. Cylindrical specimens, measuring 3 mm in diameter and 10 mm in length, were machined from these materials with the longitudinal direction parallel to the rolling direction and were heat-treated on a Formaster testing machine.

Table 1 Compositions of materials used

	Al	V	Sn	Fe	Cu	O	C	N	H
Ti-6Al-4V	6.24	4.03	—	0.16	—	0.18	0.006	0.006	0.0015
Ti-6Al-6V-2Sn	5.62	5.36	2.02	0.68	0.68	0.16	0.008	0.006	0.0010

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Ti-6Al-4V and Ti-6Al-6V-2Sn were heated and held in the β phase region at 1,050 and 1,000°C, respectively, for 20 min in vacuum at 6.7×10^{-3} Pa and were cooled at various rates to room temperature or were cooled to intermediate temperatures in the $\alpha + \beta$ region and helium gas quenched from those temperatures. To eliminate the shear component of transformation and cause diffusional transformation, Ti-6Al-4V was also subjected to the isothermal holding experiment in which it was solution treated at 1,050°C for 20 min, rapidly cooled to temperatures above the Ms point (800 to 850°C) in the $\alpha + \beta$ region, held at the temperatures for different lengths of time, and helium gas quenched from those temperatures.

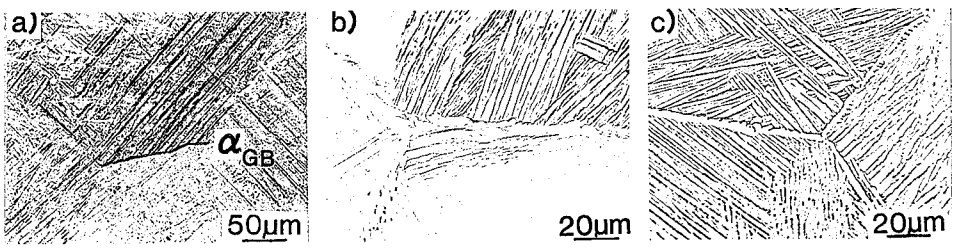
The heat-treated specimens were examined for optical microstructure on the cross section parallel to the length direction including the axis of the cylinder. Some specimens were examined under an analytical electron microscope. Thin-foil specimens were electropolished at −40°C in an electrolyte containing 90 ml perchloric acid, 525 ml butanol, and 900 ml methanol.

3. Experimental Results

Photo 1 shows the optical microstructures of Ti-6Al-4V specimens cooled at a rate of 0.5°C/s to 925 or 900°C and immediately helium gas quenched and of the specimen continuously cooled to room temperature. The α phase first preferentially precipitated at the grain boundaries of the β matrix. As the temperature then dropped, the side-plate α phase grew from the grain-boundary α phase into the β grains.

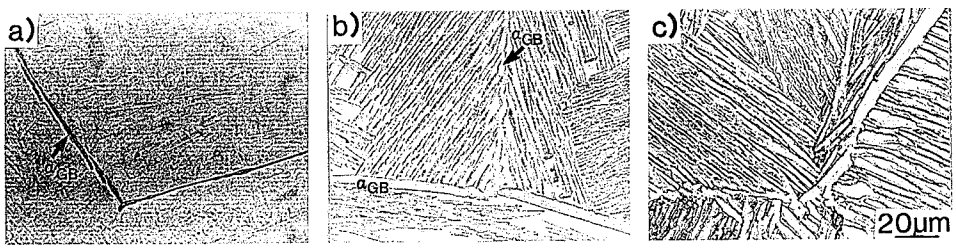
Photo 2 shows the optical microstructures of Ti-6Al-6V-2Sn specimens cooled at a rate of 0.1°C/s to 850 or 800°C and immediately helium gas quenched and of the specimen continuously cooled to room temperature. Like Ti-6Al-4V, the α phase first precipitated at the grain boundaries of the β matrix. When the specimen was continuously cooled to room temperature (**Photo 2(c)**), the side-plate α phase near the grain-boundary α phase adjoined the grain-boundary α phase. When the specimen was quenched from 800°C on cooling (**Photo 2(b)**), some side-plates of α phase were separated from the grain-boundary α phase or were necked where they adjoined the grain-boundary α phase.

Photos 3 to **5** show the optical microstructures of Ti-6Al-4V specimens rapidly cooled from 1,050°C in the β region to 940, 900 or 860°C in the $\alpha + \beta$ region, isothermally held at those temperatures, and helium gas quenched from the temperatures. At each holding temperature, the α phase was preferentially precipitated at the grain boundaries of the β matrix. As the holding time



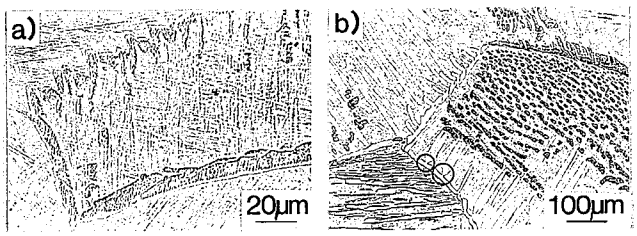
(a) Continuously cooled to 925°C and helium gas quenched (b) Continuously cooled to 900°C and helium gas quenched (c) Continuously cooled to room temperature

Photo 1 Optical microstructures of Ti-6Al-4V continuously cooled from 1,050°C at 0.5°C/s



(a) Continuously cooled to 850°C and helium gas quenched (b) Continuously cooled to 800°C and helium gas quenched (c) Continuously cooled to room temperature

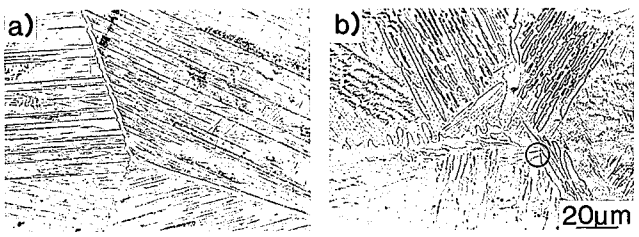
Photo 2 Optical microstructures of Ti-6Al-6V-2Sn continuously cooled from 1,000°C at 0.1°C/s



(a) Isothermally held for 600 s (b) Isothermally held for 50 ks

Photo 3 Optical microstructures of Ti-6Al-4V rapidly cooled from 1,050 to 940°C, isothermally held, and helium gas quenched

○: Local necking of side-plate α phase adjoining grain-boundary α phase



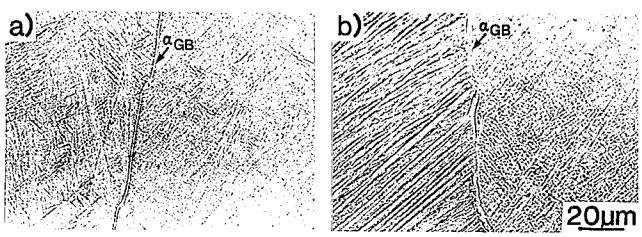
(a) Isothermally held for 30 s (b) Isothermally held for 600 s

Photo 4 Optical microstructures of Ti-6Al-4V rapidly cooled from 1,050 to 900°C, isothermally held, and helium gas quenched

○: Local necking of side-plate α phase adjoining grain-boundary α phase

extended, the side-plate α phase was formed. When the specimen was held at 940°C for 50,000 s (**Photo 3(b)**) or at 900°C for 600 s (**Photo 4(b)**), many α phase side-plates were separated from the grain boundary α phase or were necked where they adjoined the grain-boundary α phase (indicated by solid circles in each micrograph). Comparison of the specimens held for 600 s (**Photos 3(a)**, **4(b)**, and **5(b)**) shows that the size of the precipitated α phase increased with increasing holding temperatures.

Photo 6 is the transmission electron microstructure of an area near the grain-boundary α phase in the microstructure of **Photo 5(a)** and shows the microstructure observed immediately after the precipitation of the grain-boundary α phase. In the transmission electron microstructure, the interface between the grain-boundary α phase and the transformed β phase (area considered to have been the β phase before quenching and composed of the retained β phase and martensitic microstructure) was not smooth, and the grain-boundary α phase was an alternative arrangement of convex portions into the β matrix and concave portions.



(a) Isothermally held for 10 s (b) Isothermally held for 600 s

Photo 5 Optical microstructures of Ti-6Al-4V rapidly cooled from 1,050 to 860°C, isothermally held, and helium gas quenched

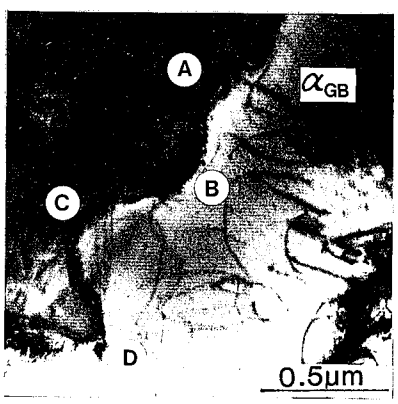


Photo 6 TEM microstructure of specimen shown in **Photo 5(a)** near grain-boundary α phase

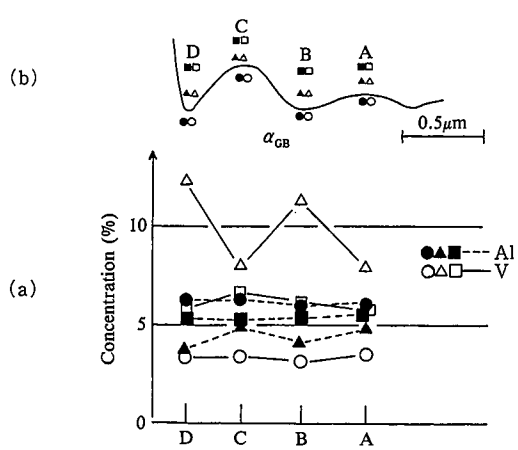


Fig. 1 Results of EDS analysis near portions A to D in **Photo 6**
Analyzed portions shown in (b) (schematic illustration of **Photo 6**)

Fig. 1 shows the results of EDS analysis near the portions A to D in **Photo 6**. In each portion, aluminum and vanadium were uniformly distributed inside the grain-boundary α phase. The vanadium concentration was extremely high in the transformed β phase adjoining the grain-boundary α phase and decreased with increasing distance from the grain-boundary α phase. In the concave portions B and C of the transformed β phase adjacent to the grain-boundary α phase, the vanadium concentration was higher than in the convex portions A and C and was more than 10 mass%.

4. Discussion

4.1 Widmanstätten structure formation mechanism

As shown in **Photos 1** to **5**, the α phase first precipitates platelike at the grain boundaries of the β matrix under the conditions where diffusional transformation is fully possible. Then, side plates are formed in aggregates within the β matrix, forming the so-called Widmanstätten structure. These observation results are reported not only for Ti-6Al-4V[6], but also for most $\alpha + \beta$ titanium alloys[7-9]. Aaronson et al.[7,10] discussed the formation mechanism of the side-plate α phase according to its similarity to hypoeutectoid steels. As indicated by Aaronson et al.[7], however, there are large differences in the formation of the Widmanstätten structure between the hypoeutectoid steels and $\alpha + \beta$ titanium alloys.

First, titanium alloys have the growth of the grain-boundary α phase arrested in an earlier stage of transformation, and the progress of transformation entirely depends on the formation of the side-plate α phase. In carbon steels, in contrast, the progress of transformation is wholly supported by the growth of grain-boundary allotriomorphs, and the Widmanstätten structure forms only under a considerably undercooled condition.

Second, the grain-boundary α phase is platelike in $\alpha + \beta$ titanium alloys and is often blocky in carbon steels. This difference may be explained as follows. In titanium alloys[11], grain growth is generally fast in the β region, and the β transus temperature of $\alpha + \beta$ titanium alloys is high. The grain size of the β matrix in $\alpha + \beta$ titanium alloys is thus larger than that of the γ matrix in carbon steels. This is because the primary α phase in carbon steels is blocky when the γ grain size is small and the α phase is formed filmlike as the γ grain size becomes large and many linear γ grain boundaries are formed[12-14]. If the grain size of the β matrix is reduced further in wrought $\alpha + \beta$ titanium alloys with a relatively large grain size of about 300 μm and many linear grain boundaries, the morphology of the Widmanstätten structure is expected to change. In this experimental study, the grain size of the β matrix after solution treatment in the β region is about 300 μm for both Ti-6Al-4V and Ti-6Al-6V-2Sn. However, in specimens manufactured by powder metallurgy where the growth of the β grains can be restricted to about 50 μm by porosities between the powder particles, the proportion of the grain-boundary α phase is increased only for the increase in the area of the β grain boundaries, and the side-plate α phase still accounts for the majority of the α phase. The resultant microstructure is basically the same as that of coarse-grained specimens[15].

Thus, the second difference cannot be explained by the grain

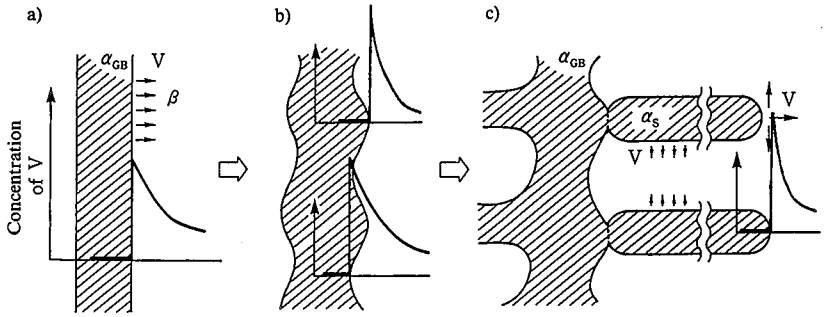


Fig. 2 Schematic illustration of formation mechanism of Widmanstätten structure in $\alpha + \beta$ titanium alloy containing β stabilizing element vanadium
Vanadium concentration and flux also shown (α_{GB}: grain-boundary α phase, α_S: side-plate α phase)

size of the β matrix or that of γ matrix alone. Based on the results of analysis by analytical electron microscopy of the area near the grain-boundary α phase in Ti-6Al-4V in the isothermal holding experiment (**Photo 6** and **Fig. 1**), the formation mechanism of the Widmanstätten structure in the $\alpha + \beta$ titanium alloys is discussed below, with attention focused on vanadium highly concentrated in the transformed β phase adjoining the grain-boundary α phase.

Fig. 2 schematically illustrates the formation behavior of the Widmanstätten structure and the change in the vanadium concentration in an $\alpha + \beta$ titanium alloy with vanadium added as a main β stabilizing element. First, the grain-boundary α phase is formed along the β grain boundaries. The elemental distribution accompanying the growth of the grain-boundary α phase creates a concentration gradient of the β stabilizing element vanadium in the β phase near the grain-boundary α phase (**Fig. 2(a)**). In this area, vanadium attains a high concentration and strongly stabilizes the β phase in the early stage of transformation. Therefore, the growth rate of the grain-boundary α phase is strongly retarded in a short time after the start of transformation.

Next, as shown in **photo 6**, concave and convex portions form in the grain-boundary α phase (**Fig. 2(b)**). This is presumably due to a sort of perturbation, but the detailed formation mechanism is not known. In the β phase adjoining the convex portion, the vanadium concentration is lower than in the convex portion, as shown in **Fig. 1**. As a result, the stability of the β phase becomes relatively low, and the convex portion alone preferentially grows. Or at the α/β interface of the convex portion, the α phase nucleates and grows into β grains, forming the side-plate α phase (**Fig. 2(c)**). There is the possibility that vanadium may concentrate again in the neighboring β phase at the end of the side-plate α phase as the side plates grow. Unlike the case where the grain-boundary α phase is formed, vanadium can diffuse in a direction normal to the growth direction, so that the vanadium concentration is not considered to become high enough to inhibit the grain growth (**Fig. 2(c)**).

The above mechanism can be used to explain that the transformation of $\alpha + \beta$ titanium alloys proceeds with the formation of not the grain-boundary α phase but the side-plate α phase and forms the Widmanstätten structure. In titanium alloy systems containing no vanadium, other β stabilizing elements are considered to play a similar role. In Ti-6Al-2Sn-4Zr-6Mo, for example, a concentration of molybdenum is confirmed in the transformed β phase near the grain-boundary α phase formed on cooling after welding[16]. Molybdenum is considered to play an important role in the formation of the Widmanstätten structure in this alloy.

4.2 Separation of side-plate α phase from grain-boundary α phase

When Ti-6Al-6V-2Sn was cooled from the β region to 800°C at a rate of 0.1°C/s, there were observed many side-plates not adjoining the grain-boundary α phase and other side-plate α phase, as shown in **Photo 2(b)**. When Ti-6Al-4V was rapidly cooled from the β region to 940 or 900°C and isothermally held at the temperatures, there also were observed many side-plates of α phase not adjoining the grain-boundary α phase or necked where they adjoined the grain-boundary α phase (see **Photos 3(b)** and **4(b)**).

It is difficult to think that the side-plate α phase not adjoining the grain-boundary α phase nucleated within the β grains. For, transgranular nucleation is often observed when the degree of undercooling is high, and heterogeneous nucleation at grain boundaries usually occurs during transformation at high temperatures where the degree of undercooling is low. This phenomenon may be rationally explained by the "separation of the side-plate α phase and the grain-boundary α phase" demonstrated by Aaronson et al.[7] in their isothermal holding experiment.

Based on this idea, the side-plate α phase necked where it adjoined the grain-boundary α phase (indicated by solid circles in **Photos 3(b)** and **4(b)**) corresponds to the initial stage of separation. This separation is considered to have resulted from the inverse transformation of the side-plate α phase adjacent to the grain-boundary α phase into the β phase in the competitive growth process. As described in 4.1, the vanadium concentrated near the grain-boundary α phase in the initial stage of transformation is thought to exert a strong influence on the separation. That is, the β stabilizing element vanadium controlling the transformation is concentrated near the grain-boundary α phase during initial transformation, and the $\alpha \rightarrow \beta$ inverse transformation is likely to occur in this area during competitive growth. If the side-plate α phase is nucleated at the interface between the grain-boundary α phase and the β phase[7,17], the α/α grain boundary should be present between the grain-boundary α phase and the side-plate α phase. The equilibrium of interfacial energies facilitates the entry of the β phase into this area and is considered to promote the separation of the side-plate α phase from the grain-boundary α phase (see **Fig. 3**). With continuous cooling transformation, the volume fraction of the α phase increases in a relatively short time with the formation of the side-plate α phase. The temporary drop in the cooling rate due to latent heat is also considered to promote the separation by localized inverse transformation.

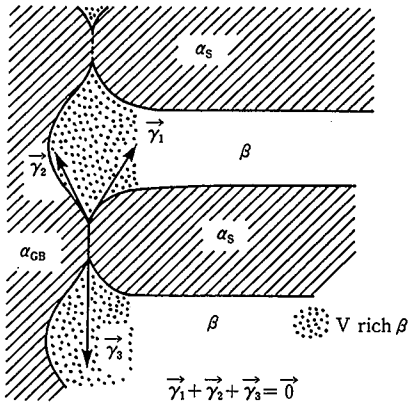


Fig. 3 Schematic illustration of separation of side-plate α phase (α_S) from grain-boundary α phase (α_{GB})

In the diagram, γ_1, γ_2, and γ_3 are interfacial energies for α_S/β interface, α_{GB}/β interface, and α_S/α_{GB} grain boundary, respectively

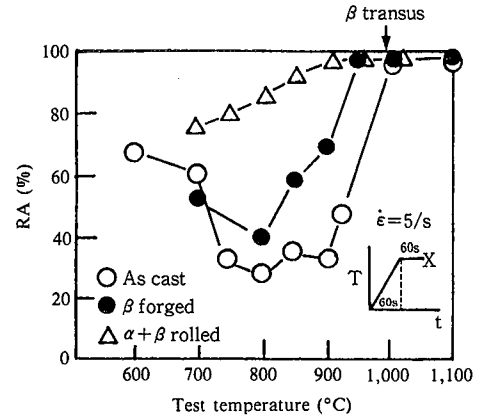


Fig. 4 Temperature dependence of reduction of area (RA) of Ti-6Al-4V

Hot tensile test conducted at an initial strain rate of 5 s^{-1} on Gleeble testing machine. ○ (as-cast): Coarse β grain size, ● (β forged): Fine β grain size, △ ($\alpha + \beta$ rolled): Fine equiaxed structure

Photos 3(a) and **4(b)** show many side-plates of α phase isolated within the β matrix apart from the grain-boundary α phase. This type of side-plate α phase is considered to have nucleated and grown at the interface between another side-plate α phase and the β phase[9,10] and to have been separated by the localized $\alpha \rightarrow \beta$ inverse transformation as observed near the grain-boundary α phase. With continuous cooling, the separated side plate connects again with the grain-boundary α phase as the volume fraction of the α phase increases on further cooling (**Photo 2(c)**).

When tensile strength and ductility or fatigue strength are required as described in the Introduction, it is necessary to transform a coarse Widmanstätten structure into a fine equiaxed structure by heavy working and annealing in the $\alpha + \beta$ region. As shown in **Fig. 4**, however, $\alpha + \beta$ titanium alloys with the Widmanstätten structure exhibit a marked loss of ductility and fracture along the grain-boundary α phase in the high $\alpha + \beta$ temperature region of (T_β − 250°C) to (T_β − 50°C)[18-20], where T_β is the β transus temperature. Several models are proposed for the fracture mechanism along the grain-boundary α phase and the ductility loss. Each model had some drawbacks and was unable to fully explain these phenomena. The author and his coworker analyzed in detail the hot ductility loss behavior of Ti-6Al-4V and proposed a model of stress concentration on the soft β phase adjacent to the grain-boundary α phase[21], or a model that is free from the drawbacks of the existing models and can fully explain the ductility loss phenomenon characteristic of the Widmanstätten structure in a specific temperature region by applying the above-mentioned separation phenomenon between the side-plate α phase and the grain-boundary α phase.

In the proposed model, when the Widmanstätten structure is reheated to 750-900°C, the inverse transformation from the α phase to the β phase preferentially occurs near the grain-boundary α phase owing to the vanadium concentrated near the grain-boundary α phase, and a "special region" is formed where the proportion of the soft β phase is locally high. The special region is lower in strength than the β matrix, so that plastic stain is likely to concentrate. As a result, voids form at the interface between the grain-boundary α phase and the β phase where many dislocations pile up or near the interface between the β phase and the side-plate α phase. A fracture arises from the coalescence of these voids. In the temperature region below 750°C, the $\alpha \rightarrow \beta$ inverse transformation is not active and the volume fraction of the β phase is low, and therefore the "special region" is not formed. Thus, the deformation is considered to be uniform to alleviate the ductility loss. In the temperature region near the β transus temperature of 990°C, the $\alpha \rightarrow \beta$ inverse transformation actively occurs in the β matrix, and the volume fraction of the β phase becomes extremely high. The region near the grain-boundary α phase is no longer the "special region", the deformation uniformly proceeds, and the ductility is improved. When the β grain size decreases, the peculiarity of the "special region" diminishes, so that the material deforms uniformly and its ductility loss is slight. An extreme example is the equiaxed structure without any grain-boundary α phase, where no ductility loss occurs from the absence of the "special region"

5. Conclusions

Continuous cooling transformation from the β region, in particular, diffusional transformation was studied using two typical $\alpha + \beta$ titanium alloys, namely, Ti-6Al-4V and Ti-6Al-6V-2Sn. The following conclusions were derived:

(1) Diffusional transformation proceeds not with the growth of the grain-boundary α phase but with the formation of the side-plate α phase. The β stabilizing element vanadium concentrated near the grain-boundary α phase during the formation of the grain-boundary α phase is considered to play an important role in this transformation behavior. In this view, a model was proposed as formation mechanism of the Widmanstätten structure.

(2) Isothermal holding at high temperatures in the $\alpha + \beta$ region and slow cooling from the β region sometimes cause the separation of the side-plate α phase from the grain-boundary α phase. This is considered a local inverse transformation to the β phase due to competitive growth, and suggests the contribution of the β stabilizing element vanadium concentrated near the grain-boundary α phase.

(3) The ductility loss of a titanium alloy with the Widmanstätten structure in a given $\alpha + \beta$ temperature region can be explained by a model that assumes that a "special region" with a high proportion of the soft β phase is locally formed along the grain-boundary α phase in the temperature region and that

the deformation is concentrated in the "special region". The "special region" is produced by the preferential inverse transformation to the β phase of the side-plate α phase adjoining the grain-boundary α phase.

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