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Quenched-in Vacancy Effect on Microstructural Evolution during Aging in β Titanium Alloy


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Abstract

A β type titanium alloy, Ti-15V-3Cr-3Sn-3Al, shows a variety of aged microstructures depending on treatments prior to aging. When the alloy is solution treated at temperatures just above the β transus, precipitation during aging is sluggish and heterogeneous. Meanwhile, the alloy solution treated at high temperatures in the β region exhibits very accelerated and very homogeneous precipitation. In the materials having larger grains, there is a tendency that fine and homogeneous precipitation takes place inside the β grains and the precipitation free zones are formed along the β grain boundaries. Such inhomogeneous microstructures can be avoided by controlling the cooling rate after the solution treatment and by employing multi-step solution treatment with special heat patterns. The evolution of the above mentioned microstructures can be explained by taking the concentration of quenched-in vacancies into account, which is determined by quenching temperature, density of vacancy sinks and cooling rate, etc.

1. Introduction

Solution treatment of β type titanium alloys is usually conducted in the β single phase temperature region above the β transus. However, there are cases in which the rate of precipitation during aging and the aged microstructures are widely varied depending on differences in solution treatment conditions such as temperature, time and cooling rate, even when the solution treatment is conducted in the β single phase region and the β phase is completely retained to room temperature. The authors carried out a systematic study on the influences of solution treatment conditions on the aging characteristics of Ti-15V-3Cr-3Sn-3Al, a typical β type titanium alloy, and made it clear that vacancies existing at the solution treatment temperature were partially quenched-in and brought to room temperature or the aging temperature and that the quenched-in vacancies had a remarkable influence on precipitation characteristics during aging[1-5].

Table 1 outlines the result of the study. The concentration of the quenched-in vacancies tends to be high in samples quenched from high temperature or having small number of dislocations and grain boundaries acting as vacancy sinks, and in contrast, it tends to be

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Table 1 Relationship between characteristics of aged microstructures and quenched-in vacancies of β type titanium alloys

Concentration of quenched-in vacancies	High	Low
Quenching temperature	High	Low
Concentration of vacancy sinks	Low · Large grain size · Low dislocation density	High · Small grain size · Relatively high dislocation density (recovered structure, light plastic deformation)
Precipitation sites	Compounds composed of excess vacancies and solute elements (?) β zone (β')	Dislocations, grain boundaries, twin boundaries, etc.
Aged microstructures	Homogeneous	Heterogeneous
	≦350°C: aggregate of fine particles (α,ω) >400°C: acicular blocks (α)	
Rate of precipitation	Rapid (especially ≦ 350°C)	Slow

low when samples having dislocations in a high concentration or fine grains are quenched from temperature in the lower β region, that is, just above the β transus. Though not written in Table 1, the cooling rate is another significant influencing factor as will be explained in section 6.

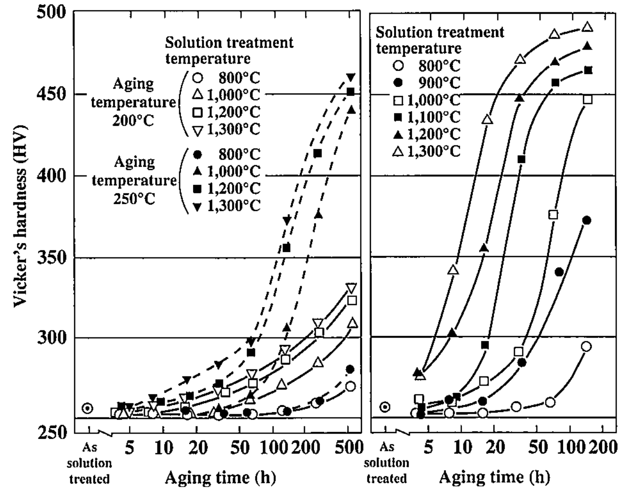
Thus, when samples having different concentrations of excess vacancies are aged, the aged microstructure and the rate of precipitation are widely different : whereas macroscopically very homogeneous structure forms in a short time when there are many excess vacancies in the material, normal precipitation proceeds slowly at dislocations and grain boundaries acting as precipitation sites when there are a small number of excess vacancies. No direct evidence has yet been found with regard to the reasons for the accelerated aging and formation of the homogeneous microstructure of the former case. However, the phenomenon is probably caused by the formation of compounds composed of the vacancies and solute elements (especially interstitial impurity elements), rather than the excess vacancies helping the diffusion of alloying elements. It is suggested that the compounds may be identical to the zone called β' [3].

This paper introduces the variety of the aged microstructures of Ti-15V-3Cr-3Sn-3Al and explains the formation mechanism of the aged microstructures based on the findings listed in Table 1.

2. 1-step Solution Treatment

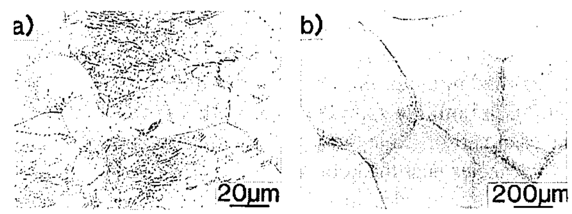
Initially, aging characteristics are introduced regarding hot rolled Ti-15V-3Cr-3Sn-3Al alloy plates (having a thickness of 10 mm and the β transus of 760°C) after a normal 1-step solution treatment comprising the heating, holding and quenching.

Fig. 1 shows age hardening curves of samples solution treated at 800 to 1,200°C for 30 min, water quenched and then aged at 200 to 250°C (Fig. 1 (a)) and 300°C (Fig. 1 (b)). Although all the samples were solution treated at temperatures within the same β region, they show quite different hardening behaviors during aging: the higher the solution treatment temperature the quicker the hardening during aging proceeds. For instance, when the aging temperature is 300°C (Fig. 1 (b)), while the sample solution treated at 800°C, just above the β transus, barely begins to harden after aging for 100 h or more,



(a) Aging temperature : 200 to 250°C (b) Aging temperature : 300°C

Fig. 1 Age hardening behaviors of samples solution treated (800 to 1,300°C, 30 min) and water quenched



(a) 800°C, 30 min, water quenching + 300°C × 128 h (b) 1,200°C, 30 min, water quenching + 300°C × 64 h

Photo 1 Aged microstructures of samples 1-step solution treated and aged at 300°C

the sample solution treated at 1,200°C begins to harden after only 4 h of aging and the age hardening is completed in about 100 h.

Photo 1 shows aged microstructures at 300°C of the samples solution treated at 800 and 1,200°C. Whereas the α phase has barely commenced to precipitate in the sample solution treated at 800°C (Photo 1 (a)) after aging for 128 h, it has precipitated in the entire section of the sample solution treated at 1,200°C (Photo 1 (b)) after aging for 64 h. What is more, while the precipitation takes place heterogeneously at grain boundaries and strained portions inside grains in the case of the sample solution treated at 800°C, the extremely fine α phase which is scarcely discernible with an optical microscope forms very homogeneously in the whole sample solution treated at 1,200°C. This is probably because, in the sample solution treated at 800°C, as a result of a low quenching temperature and small grain size (many β grain boundaries acting as vacancy sinks), most of the vacancies existent at 800°C disappeared during the cooling. Furthermore, in contrast, in the sample solution treated at 1,200°C, many of the vacancies were quenched-in and survived during cooling to room temperature since a large number of vacancies existed at 1,200°C and β grains were large (fewer β grain boundaries acting as the vacancy sinks).

For more microscopic forms of the precipitation of the α phase (formed during aging at 300°C or higher) and the ω phase (formed during aging at 250°C or lower) of the latter material, see TEM photomicrographs in the reference literatures 1) to 5).

3. 2-step Solution Treatment

Fig. 2 shows a heat pattern of a 2-step solution treatment. A Ti-15V-3Cr-3Sn-3Al plate of 10 mm in thickness, which is the same as the 1-step solution treated material described in section 2, was solution treated at 1,200°C for 30 min, air cooled to 800°C, held at 800°C for 30 min and then water quenched. The microstructure of the sample aged at 300°C is shown in **Photo 2**. Whereas fine precipitates of the α phase form homogeneously inside the β grains at an early stage of the aging (Photo 2 (b)) like the sample 1-step solution treated at 1,200°C (Photo 1 (b)), little precipitation was observed near the grain boundaries even after aging for 64 h, and zones free from precipitates were created (Photo 2 (c)). Although the 2-step solution treated sample consists of coarse grains about 500 μm in size like the sample 1-step solution treated at 1,200°C, the forms of precipitation differ remarkably between the two. Reasons for this are considered as follows:

In both the 1-step solution treated sample treated at 1,200°C and the 2-step solution treated sample, the grain size is large and the quantity of grain boundaries acting as the vacancy sinks is small. Therefore, the vacancies are likely to be quenched-in during the quenching. However, it is clear that the β grain boundaries act as the vacancy sinks, and a considerable number of vacancies ought to have been absorbed in the grain boundaries and disappeared during the quenching in both the samples. During this process, even though vacancies are absorbed in the β grain boundaries and the concentration of vacancies near the boundaries is lowered during the cooling, vacancies are quenched-in in a high concentration in the entire sample of the 1-step solution treated material because it was quenched from 1,200°C, which is a very high quenching temperature where the equilibrium vacancy concentration is very high, as many fresh vacancies are supplied from inside the grains to the area near the grain boundaries. On the other hand, in the 2-step solution treated material, since it was quenched from 800°C where the equilibrium vacancy concentration is low, fresh vacancies are not sufficiently supplied from inside the grains to the area near the grain boundaries where vacancy concentration is lowered during the quenching and, as a consequence, vacancies are depleted near the grain boundaries, forming the precipitation free zones during the aging process.

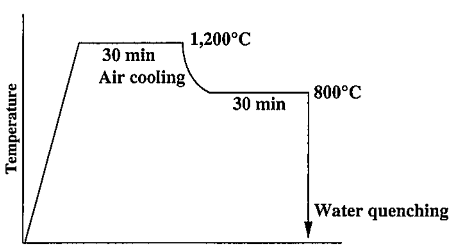
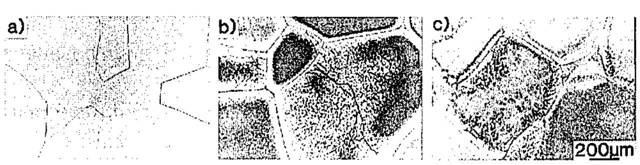


Fig. 2 **Heat pattern of 2-step solution treatment (1,200°C, 30 min, air cooling to 800°C + 800°C , 30 min, water quenching)**



(a) As solution treated (b) Aged microstructure (aged at 300°C for 32 h) (c) Aged microstructure (aged at 300°C for 64 h)

Photo 2 Microstructures of 2-step solution treated samples after solution treatment and aging

4. 3-step Solution Treatment

Next, a case that dislocations served as the vacancy sinks is introduced. **Fig. 3** shows a heat pattern of a 3-step solution treatment, in which materials are solution treated at 1,200°C for 30 min, water quenched, fully aged once at 500°C, then solution treated again at 800°C, just above the β transus, for 30 min and then water quenched. The sample used in the test of this heat treatment was a Ti-15V-3Cr-3Sn-3Al plate of 10 mm in thickness, which is the same material described in sections 2 and 3. During the aging at 500°C, which lasted for 96 h, the α phase precipitated all over the sample, and during the precipitation process, dislocations were created in the matrix β phase together with the precipitation of the α phase, and the dislocations formed recovered microstructure during the final re-solution treatment[1-5]. The precipitation and hardening during aging of the samples having the recovered structure are totally different from those of the 1-step solution treated sample treated at 1,200°C and the 2-step solution treated sample having the same grain size, and are rather similar to those of the 1-step solution treated sample treated at 800°C.

A hardening curve of the 3-step solution treated sample during aging at 300°C is shown in **Fig. 4**. As seen in the figure, its age hardening is remarkably slower compared with the 1-step solution treated sample treated at 1,200°C, but pretty close to that of the 1-step solution treated sample treated at 800°C. As is shown in **Photo 3** (a), the precipitation of the α phase in the 3-step solution treated sample is yet in the initial stage even after aging at 300°C for 128 h, considerably slower than that of the 1-step solution treated sample

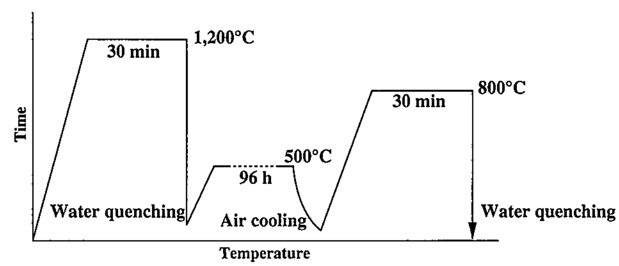


Fig. 3 **Heat pattern of 3-step solution treatment (1,200°C, 30 min, water quenching + 500°C, 96 h, air cooling + 800°C, 30 min, water quenching)**

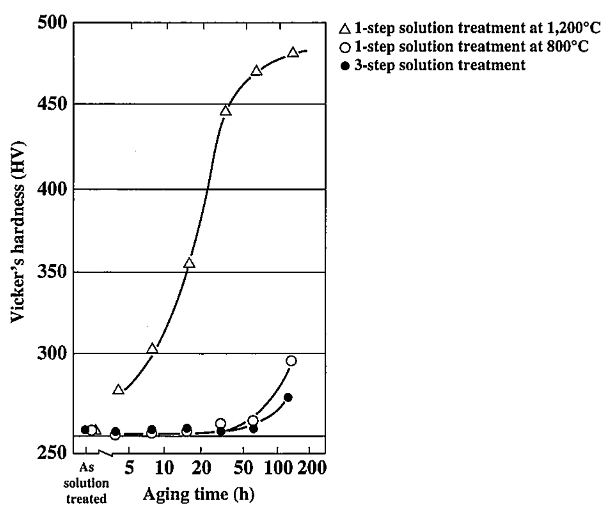
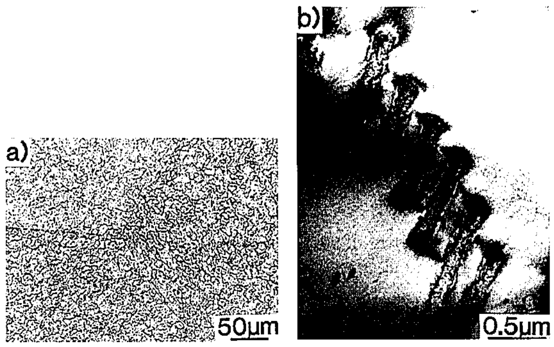


Fig. 4 **Age hardening behavior at 300°C of 3-step solution treated sample (compared with 1-step solution treated samples treated at 800 and 1,200°C)**



(a) Optical micrograph (b) TEM micrograph

Photo 3 Optical and TEM micrographs of sample 3-step solution treated and aged at 300°C for 128 h

treated at 1,200°C and nearly the same as that of the 1-step solution treated sample treated at 800°C. The reason for this is considered that dislocation networks (sub-boundaries) formed in the recovered structure during the 3-step solution treatment serve as the vacancy sinks and, thus, most of the vacancies disappear during quenching without being quenched-in. It should be noted that the dislocations also act as precipitation sites for the α phase. In fact, as seen in Photo 3 (b), the α phase precipitates at the dislocations which formed networks. Consequently, the reason why the age hardening of the 3-step solution treated sample is slow is considered that the dislocations in a comparatively high concentration acted more as the vacancy sinks than the precipitation sites.

5. Influence of Plastic Deformation

A case that dislocations are included in the matrix β phase in a comparatively high concentration was explained in section 4. Similar cases can be seen also when a small amount of plastic strain is imposed on materials.

Photo 4 is the microstructure of a sample prepared as follows: a 1-step solution treated material treated at 1,200°C, having a large quantity of excess vacancies, was hit on a surface with a punch and then aged at 400°C for 4 h. While the precipitation of the α phase is accelerated in the subsurface portion subjected to strong plastic deformation of the punch and also the inner portion, the precipitation is slow in the portions in between, which underwent only a little plastic strain, and also near the twin boundaries, in which precipitation free zones were observed. Whereas the quick precipitation during aging in the inner portion is due to the high concentration of the quenched-in vacancies as explained in section 2, what happened in the portions in which the precipitation is sluggish is probably that the dislocations and twin boundaries introduced by the plastic deformation served as the vacancy sinks during the early stage of the aging, wiping out the excess vacancies in the portions. Naturally, the excess vacancies in the subsurface portions also ought to have disappeared. However, dislocations were created in a high concentration by the strong plastic deformation, making up for the disappeared vacancies, and they served as the precipitation sites and accelerated the precipitation during the aging.

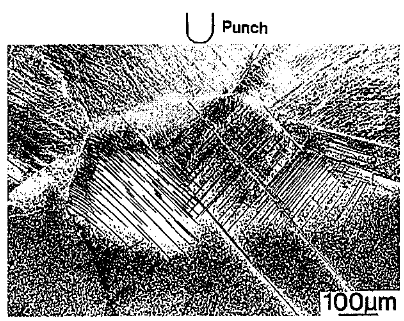


Photo 4 Microstructure of 1-step solution treated sample treated at 1,200°C for 30 min, water quenched, punched on a surface and aged at 400°C for 4 h

6. Anomalous Structure in Thick Materials

β type titanium alloys are widely used in the forms of thin gauge sheets and thin wires thanks to their excellent cold workability. However, they are also used in considerable quantities in the forms of medium to thick plates and bars by taking advantage of their excellent strength. When thick materials of the alloys are solution treated and aged, anomalous eyeball-like structures sometimes appear especially in subsurface portions.

Photo 5 shows an example of the subsurface microstructure of a thick plate of 12.5 mm in thickness, solution treated at 800°C for 30 min, water quenched and aged at 400°C. At the initial stage of the aging (Photo 5(a)), the fine α phase precipitates homogeneously in the β grains only, and its precipitation near the grain boundaries is markedly slower in comparison. As the aging proceeds (Photo 5 (b)), the α phase precipitates also near the β grain boundaries but its morphology is different from the precipitation inside the β grains, and the eyeball-like anomalous structures still remain. The eyeball structures are observed only in the subsurface portions and, besides the quenching temperature and the vacancy sinks, the cooling rate is suspected to have a strong influence upon their formation. This presumably means that, in the subsurface portions where the cooling rate is high, some of the vacancies in the β grains cannot reach grain boundaries, which act as the sinks, during the water quenching after the solution treatment. Therefore, they are quenched-in inside the β grains, thereby helping the fine α phase precipitate homogeneously in the β grains. On the other hand, in the inner portion of the material away from the surfaces, the cooling rate is slower compared to the subsurface portions, consequently the excess vacancies in the grains can easily reach the β grain boundaries during the cooling and, thus, most of them disappear, making the α phase precipitation slower.

If the above hypothesis is true, formation of the anomalous structures ought to be controlled by lowering the cooling rate. On this basis, we changed the medium of the cooling after the solution treatment from water to air, and the anomalous eyeball structures ceased to appear at all in the subsurface portions as shown in **Photo 6**, and nearly homogeneous aged microstructure was obtained from the subsurface portion through to the inner portion.

The thick materials, in which the anomalous eyeball structures often appear, are usually used after hot rolling and solution treatment, and in most cases, the hot working is not intensive. Besides, the solution treatment is often conducted at a high temperature or for

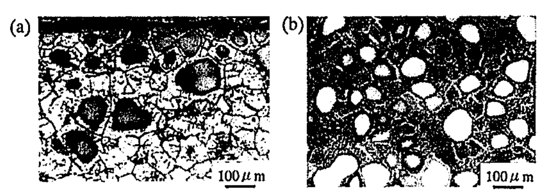


Photo 5 Subsurface microstructures of sample plate 12.5 mm thick solution treated at 800°C for 30 min, water quenched and aged at 480°C (aging time: (a) 1 h, (b) 16 h)

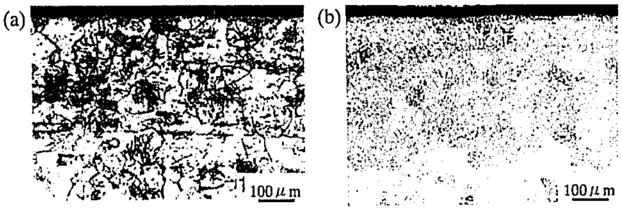
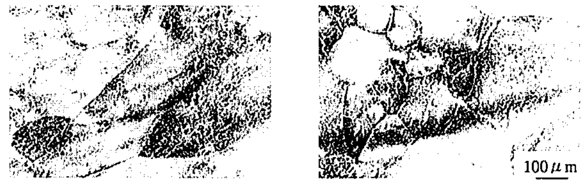


Photo 6 Subsurface microstructures of plate of 12.5 mm thick solution treated at 800°C for 30 min, air cooled and aged at 480°C (aging time: (a) 1 h, (b) 8 h)



(a) Weld metal (b) Heat affected zone

Photo 9 Microstructures of samples welded by keyhole plasma arc welding and aged at 510°C for 16 h

a long period of time in order to obtain fully recrystallized materials. It is, therefore, suspected that the reason why the eyeball-like structures frequently appear especially in thick materials is that the grain size of the thick materials tends to be larger than that of cold-worked thin gauge sheets and thin wires and as a consequence, the concentration of the vacancy sinks becomes lower and the excess vacancies are more easily quenched-in.

In the case of the thick plate of 12.5 mm in thickness shown in Photos 5 and 6, the anomalous structures were successfully prevented through the air cooling after the solution treatment. However, 12.5 mm is nearly the upper limit of the thickness range where the α phase is prevented from precipitating in the thickness center portion by air cooling. For this reason, when the thickness is any larger than this, materials have to be water quenched after the solution treatment. The 3-step solution treatment explained in section 4 is recommended for such materials. As shown in Fig. 3, materials are water quenched at the final stage of the 3-step solution treatment, but quenching-in of a great quantity of excess vacancies does not take place, since sub-boundaries serving as the vacancy sinks are well developed, and thus the eyeball structures are prevented from forming.

Photo 7 shows the microstructure of a hot forged bar of 25 × 25 mm in section aged at 480°C after solution treatment at 800°C for 1 h and water quenching. In contrast, **Photo 8** shows the microstructure of another sample of the same specification but aged after the 3-step solution treatment, wherein the eyeball-like aged microstructures, which appeared through the normal solution treatment + quenching route, did not appear at all, evidencing the effect of the 3-step solution treatment to suppress their formation.

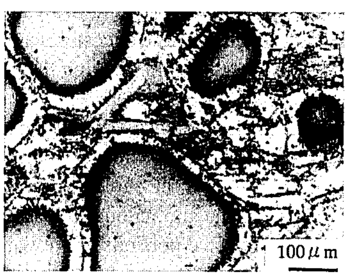


Photo 7 Microstructure of hot forged bar of 25 × 25 mm in section solution treated at 800°C for 1 h, water quenched and aged at 480°C for 10 min

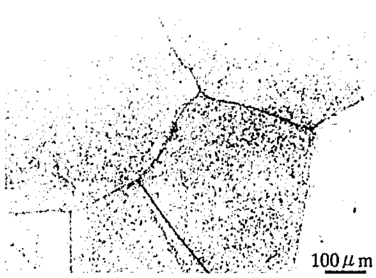


Photo 8 Microstructure of hot forged bar of 25 × 25 mm in section 3-step solution treated (800°C, 20 min, water quenching + 540°C, 24 h, air cooling + 800°C, 20 min, water quenching) and aged at 510°C for 16 h

7. Weld Metal and Heat Affected Zones

Since weld metals and heat affected zones (HAZ) are rapidly cooled from high temperature after welding and the grains are large there, vacancies are likely to be quenched-in in high concentration according to Table 1. Consequently, when a weld joint undergoes the aging, the anomalous structures as described in section 6 may form. To confirm this, Ti-15V-3Cr-3Sn-3Al plates of 10 mm in thickness, solution treated at 800°C for 30 min and then air cooled, were welded by keyhole plasma arc welding (1 pass) and then subjected to the aging.

Photo 9 shows the aged microstructure of the weld metal (Photo 9 (a)) and that of heat affected zone (Photo 9 (b)). No trace of the eyeball-like structures was seen in either of them. This is presumably due to the plastic strain created during the welding work as seen in the micrographs and lattice defects such as dislocations acting as strong vacancy sinks.

8. Summary

As explained above, solution treatment in the β single phase temperature region can bring about a wide variety of aged microstructures depending on the treatment conditions and the size and production history of treated materials. It is well known that mechanical properties of a material are strongly affected by its microstructure and therefore, in actual application of solution treated and aged β type titanium alloys, it is necessary to fully study not only the conditions of the aging treatment but also the conditions of the solution treatment. In particular, the soft precipitation free zones and the area in which the extremely fine particles precipitate such as eyeball-like anomalous structures, which are hardened and prone to be brittle, are not desirable for general applications except in special cases. Attention has to be paid in setting the conditions for working and heat treatment including solution treatment so that the undesirable structures may not form.

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