Effect of Solutioning Conditions on Aging Response in Ti-15V-3Cr-3Sn-3Al[†]

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An effect of the solutioning conditions on the aging response (precipitation, age hardening) in a β type titanium alloy, Ti-15V-3Cr-3Sn-3Al, is examined.

The aging response is strongly affected by the solutioning conditions and closely related to the concentration of quenched-in vacancies, which is a function of the quenching temperature and the density of vacancy sinks such as β grain boundaries, dislocations, etc. For example, the ω ($\leq 250^\circ\text{C}$) and the α ($300 \sim 350^\circ\text{C}$) precipitations and the age hardening are greatly accelerated in the specimens in which a large amount of quenched-in vacancies are contained, i.e. the specimens quenched from high temperatures and/or with a small density of vacancy sinks. Furthermore, the α phase precipitates very homogeneously inside the β grains at the aging temperatures between 300 and 500°C . However, the precipitation delays and the denuded zones are sometimes observed in the area in which vacancy sinks exist, e.g. in the vicinity of the β grain boundaries or the isolatedly formed twins, or in the area in which dislocations are introduced due to the weak plastic deformation.

In the specimens quenched from lower temperatures in the β region and having a smaller β grain size or a slightly higher density of dislocations, the delay of the aging response is significant and the α phase precipitation is heterogeneous. These phenomena are considered to be caused by a stronger effect of small amount of excessive vacancies, which is due to the relatively high density of the vacancy sinks and the lower quenching temperature, rather than the effect of the β grain boundaries and dislocations as precipitation sites.

(Received October 30, 1992)

Keywords: β titanium alloy, solution treatment, aging, quenched-in vacancy, sink, grain boundary, dislocation, age hardening, precipitation

I. Introduction

A most popular β type titanium alloy, Ti-15V-3Cr-3Sn-3Al, is known for excellent cold workability and uniform mechanical properties with a less property scatter. Like other β type alloys, high strength can be obtained by the following procedures; solution treatment above the β transus, rapid cooling by which the metastable β phase retains at room temperature, and subsequent aging in the $\alpha + \beta$ two phase region by which the α phase precipitates in the β matrix. There have been detailed studies about the influence of aging conditions on the α precipitation and the mechanical properties, in which the strong relationship between them has been reported⁽¹⁾⁻⁽⁴⁾. However, in those studies, the temperature just above the β transus was chosen as the solutioning temperature probably in order to suppress the β grain growth and the oxidation in the case of the heat treatment in the air and to reduce the energy used. Therefore, less attention has been paid to the effect of solutioning conditions on the aging response. Even if the studies on the other β type alloys are included, very limited research work on this issue can be seen⁽⁵⁾. However, some recent experimental results suggest that the influence of the solutioning conditions on the aging response is significant⁽⁶⁾⁻⁽⁸⁾.

Hence, it is very important to conduct a systematic study on this issue from a viewpoint of controlling the mechanical property of the aged materials.

In the present study, the aging response of Ti-15V-3Cr-3Sn-3Al solution treated under the various conditions is investigated and an effect of the solutioning conditions on the aging response is discussed.

II. Experimental Procedures

The material used was Ti-15V-3Cr-3Sn-3Al which was double melted by the vacuum arc remelting. The composition of the ingot is shown in Table 1 and the β transus is 760°C . The ingot was forged at 1100°C and hot rolled at 900°C to a plate of 12 mm in thickness. 1 mm from each surface of the plate was removed by grinding, resulting in the plate of 10 mm in thickness, and the plate was cut into small pieces of 100 mm $\times$ 70 mm, and then, they were solution treated in the air with the various patterns shown in Fig. 1: the 1-step solution treatment (Fig. 1(a)) in which the specimens were heated to $800 \sim 1300^\circ\text{C}$, held for 30 min and water quenched, the

Table 1 Composition of an alloy used.

(mass%)									
Ti	V	Cr	Sn	Al	Fe	O	C	N	H
Bal.	15.0	3.03	3.09	3.32	0.06	0.08	0.004	0.012	0.001

[†] This paper was originally published in Japanese in J. Japan Inst. Metals, 55 (1991), 1063.

Fig. 1 Patterns of the solution treatment used in the experiment. (a) 1-step solution treatment (800~1300°C, 30 min, water quenching), (b) 2-step solution treatment (1200°C, 30 min, air cooling to 800°C+800°C, 30 min, water quenching), (c) 3-step solution treatment (1200°C, 30 min, water quenching+500°C, 96 h, air cooling+800°C, 30 min, water quenching).

2-step solution treatment (Fig. 1(b)) which is 1200°C, 30 min, air cooling to 800°C+800°C, 30 min, water quenching, and the 3-step solution treatment (Fig. 1(c)) which is 1200°C, 30 min, water quenching+500°C, 96 h, air cooling+800°C, 30 min, water quenching. The purposes of the 2-step and 3-step solution treatments are to make equal some factors which are considered to affect the aging response and to compare the effect of other specific factors. The details will be explained later in the experimental results or discussion. After the solution treatments, the specimens were ground again by about 1.5 mm from each surface, resulting in 7 mm in thickness, and subdivided into small blocks of 10 mm × 10 mm × 7 mm. These small block specimens were aged at 200~500°C for 1 to 512 h in the air. Some of the specimens which were 1-step solution treated at 1200°C were struck on their surfaces with a punch before aging. Optical microstructural observations and Vickers hardness measurements (5 kg load) were performed for the central area of the specimens. For the 1-step solution treated specimens at 800°C, which had about 10% of the unrecrystallized area, the hardness was measured in the recrystallized area. TEM observations were also conducted for some specimens, where the thin foil samples were prepared by electropolishing at -40°C using the electrolyte consisting of 95 g NaClO₄, 900 cm³ CH₃OH and 525 cm³ C₃H₇OH.

As it was feared that the contamination of interstitials especially oxygen during solution treatment at high temperatures affected the aging response, the oxidation inhibitor⁽⁹⁾ was coated on the specimens in the solution treatments which include the heating to the temperatures higher than 1000°C in their patterns so that the oxygen contamination was suppressed. Table 2 shows the compositions of interstitial elements in the as-hot rolled plate and the as solution treated specimens (after removing

their surface layers). Oxygen concentration was unchanged compared with the ingot shown in Table 1, which demonstrates that no contamination of oxygen occurred.

III. Experimental Results

1. 1-step solution treatment

The age hardening behaviors in the 1-step solution treated specimens at various aging temperatures are shown in Fig. 2(a)–(f). The hardness of the as-solution treated specimens was equally HV255 in spite of the different solutioning temperatures. However, the age hardening behaviors were not always similar. In particular, at the aging temperatures lower than 350°C, quite different age hardening behaviors were observed i.e. the higher solutioning temperature led to the faster age hardening. For example, the age hardening began only in 16 h at 200°C in the specimens solution treated at 1300°C (Fig. 2(a)), which is referred as the “1300°C (1-step) solution treated specimens” from now on. The strongest effect of the solutioning temperatures on the age hardening appeared at the aging temperature of 300°C (Fig. 2(b)). For example, the hardness of the specimen aged for 64 h at 300°C after the 800°C solution treatment was only HV260, which means that 64 h is just in a very early stage of aging, while the 1300°C solution treated specimens already reached HV490. On the other hand, the very strong influence of the solutioning temperatures was not seen at the aging temperatures higher than 400°C (Fig. 2(d), (e) and (f)).

Optical micrographs of the as solution treated specimens are shown in Fig. 3. All of the specimens were composed of only the recrystallized β phase except the 800°C solution treated specimen which had about 10% of unrecrystallized β grains. The recrystallized grain size was about 40 μ m in the 800°C solution treated specimen, and it increased with increasing solutioning temperature and reached about 700 μ m in the 1300°C solution treated specimens.

Figures 4–8 show the aged microstructures. Figure 4 is a TEM micrograph of the specimen aged at 250°C for 256 h after solution treated at 1200°C. Fine precipitates were found extensively in the specimen and the diffraction pattern identified that they are the ω phase.

The α precipitation was detected at the aging tempera-

Table 2 Concentrations of O, N and H in an as rolled and two kinds of as solution treated materials. No contaminations due to the high temperature heat treatment are detected.

	(mass%)		
	O	N	H
As rolled	0.09	0.010	0.005
As 1200°C 1-step solution treated	0.06	0.013	0.006
As 3-step solution treated	0.08	0.012	0.005

Fig. 2 Age hardening behavior in the 1-step solution treated specimens. Aging temperatures are (a) 200 and 250°C, (b) 300°C, (c) 350°C, (d) 400°C, (e) 450°C and (f) 500°C.

Fig. 3 Optical micrographs of the as 1-step solution treated specimens. Temperatures of solution treatment are (a) 800°C, (b) 900°C, (c) 1000°C, (d) 1100°C, (e) 1200°C and (f) 1300°C.

Fig. 4 The ω precipitation in the specimen aged at 250°C for 256 h after the 1-step solution treatment at 1200°C (beam $\parallel [1\bar{1}0]_\beta$).

Fig. 5 Optical micrographs of the specimens aged at 300°C (a) for 128 h after the 1-step solution treatment at 800°C and (b) for 64 h after the 1-step solution treatment at 1200°C .

tures higher than 300°C as shown in another work⁽¹⁰⁾. However, the morphologies and the precipitation kinetics were extremely different depending on the solutioning temperatures.

Optical micrographs of the specimens aged at 300°C after solution treated at 800 and 1200°C are shown in Fig. 5. In the 800°C solution treated specimen (Fig. 5(a)), only a small amount of the α phase precipitated heterogeneously at the β grain boundaries and in the β grains for the aging time of 128 h. Meanwhile, a large amount of the α phase already precipitated homogeneously in the extensive area of the specimen for the aging time of only 64 h after solution treated at 1200°C (Fig. 5(b)), which corresponds to the fast age hardening behavior (Fig. 2(b)). The microstructures of

the specimens aged at 300°C after solution treatment at other solutioning temperatures ($900\sim 1100^\circ\text{C}$ and 1300°C) were similar to that in the 1200°C solution treated and 300°C aged specimen although the precipitation was faster in the specimens solution treated at higher temperatures, which also corresponds to the age hardening behavior (Fig. 2(b)).

Figures 6–8 show the optical microstructures of the specimens aged at 500°C for 4–32 h after solution treated at 800 , 1000 and 1200°C , respectively. In the 800°C solution treated specimen (Fig. 6), the α phase precipitated preferentially at the β grain boundaries or heterogeneously in the β grains. Meanwhile, in the 1000°C (Fig. 7) and 1200°C (Fig. 8) solution treated

Fig. 6 Optical micrographs of the specimens aged at 500°C for (a) 4 h, (b) 8 h and (c) 32 h, after the 1-step solution treatment at 800°C . Arrows show the unrecrystallized β grains.

Fig. 7 Optical micrographs of the specimens aged at 500°C for (a) 4 h, (b) 8 h and (c) 32 h, after the 1-step solution treatment at 1000°C.

Fig. 8 Optical micrographs of the specimens aged at 500°C for (a) 4 h, (b) 8 h and (c) 32 h, after the 1-step solution treatment at 1200°C.

specimens, the α phase precipitated not only at the β grain boundaries but also in the β grains very homogeneously. These morphological features were almost the same as those of the specimen aged at 300°C. The kinetics of the precipitation were not so different between the specimens solution treated at the different temperatures as seen at the aging temperature of 300°C. In other words, the slightly faster precipitation was observed in the specimens solution treated at higher temperatures. These tendencies also corresponded to the age hardening behavior shown in Fig. 2(f). It is noticeable that the denuded zones were formed near the β grain boundaries in the 1000 and 1200°C solution treated specimens. In the 1200°C solution treated specimens, it disappeared as the α precipitation proceeded, while it still remained in 32 h in the 1000°C solution treated specimen. The precipitation behavior in the 900 and 1100°C solution treated specimens was similar to that in the 1000°C solution treated one, and that in the 1300°C solution treated specimen was similar to that in the 1200°C solution treated one.

2. 2-step solution treatment

Figure 9 shows optical microstructures of the as 2-step solution treated specimen (Fig. 9(a)) and the subsequently aged specimens at 300°C (Fig. 9(b) and (c)). The β grain size was about 500 μm which was almost the same as that of the 1200°C 1-step solution treated specimen (Fig. 3(e)). Considerably homogeneous precipitation was seen inside the β grains in the relatively short aging time like the 1200°C solution treated specimen. However, the denuded zones were formed in the vicinity of the β grain boundaries. By the CMA(EPMA) analyses conducted for the as solution treated specimen, it was confirmed that the solute elements are uniformly distributed and there is no segregation.

The age hardening behavior at 300°C in the 2-step solution treated specimens is shown in Fig. 10, in which those in the 800 and 1200°C 1-step solution treated specimens are also shown for comparison. Hardness measurement was conducted separately for the inside of the β grains and for the area near the β grain boundaries. The age

Fig. 9 Optical micrographs of the 2-step solution treated specimens. (a) As solution treated, (b) aged at 300°C for 32 h and (c) aged at 300°C for 64 h.

Fig. 10 Age hardening behavior at 300°C in the 2-step solution treated specimens. Hardness measurements are conducted for the inside of the β grains and the vicinity of the β grain boundaries separately. In the figure, the age hardening behavior in the 1-step solution treated specimens at 800 and 1200°C is also plotted for reference.

hardening near the grain boundaries was slow as well as that in the 800°C 1-step solution treated specimen, which corresponds to the precipitation delay and the formation of the denuded zone. Meanwhile, corresponding to the

rapid precipitation, the very fast age hardening was observed inside the β grains compared with the 800°C 1-step solution treated specimen, although it is not so fast as the 1200°C 1-step solution treated specimen.

3. 3-step solution treatment

The as-solution treated microstructures of the 3-step solution treated specimen are shown in Fig. 11. The β grain size was about 500 μm as indicated in the optical micrograph (Fig. 11(a)), which is almost the same as that of the 1200°C 1-step and 2-step solution treated specimens. As shown in the TEM micrographs (Fig. 11(b) and (c)), relatively high density of dislocations were included in the β grains and many of them form the rows or networks.

The age hardening behavior at 300°C in the 3-step solution treated specimens is shown in Fig. 12 in which that of the 800 and 1200°C 1-step solution treated specimens is also drawn for comparison. The age hardening in the 3-step solution treated specimen was very sluggish compared with the 1200°C 1-step solution treated one and it was almost equal to that in the 800°C 1-step solution treated one.

4. Effect of plastic deformation

Figure 13 is an optical micrograph of the specimen which was 1200°C 1-step solution treated, plastically deformed by striking the surface with a punch, and aged at 400°C for 4 h. Inside the specimen in which little strain was given and in the area near the surface in which much strain was added, a great deal of α precipitation was observed. On the other hand, the precipitation delay was observed in the area between them in which an intermediate amount of plastic strain was added. In the area near the isolatedly formed twins (shown by the arrows in Fig. 13), the precipitation delay was also observed.

Fig. 11 (a) Optical, (b) and (c) TEM micrographs of the as 3-step solution treated specimen.

Fig. 12 Age hardening behavior at 300°C in the 3-step solution treated specimens. In the figure, the age hardening behavior in the 1-step solution treated specimens at 800 and 1200°C is also plotted for reference.

Fig. 13 An effect of the plastic deformation after the 1-step solution treatment at 1200°C on the α precipitation (aged at 400°C for 4 h).

IV. Discussion

1. Effect of quenched-in vacancies on aging response

As explained in the experimental results, the precipita-

tion and age hardening behavior vary dramatically depending on the solutioning conditions. Such a kind of phenomenon was also observed in another β type alloy, Ti-5Mo-5V-8Cr-3Al, which has the β transus of 750°C, and the relationship with the quenched-in vacancies was pointed out⁽⁵⁾. Hida and Sukedai⁽¹¹⁾ also pointed out the possibility of the existence of the quenched-in vacancies in Ti-20 mass%Mo and they emphasized that it is necessary to pay more attention to the role of the quenched-in vacancies in the titanium alloys as well. In this research work, it should be proper that the most of the phenomena shown in the experimental results are related to the quenched-in vacancies. The reason is that the α precipitation is extremely delayed and the denuded zones are easily formed in the area in which vacancy sinks such as the β grain boundaries, dislocations and twin boundaries exist. Figs. 7-9 are the examples of the precipitation delay and the denuded zones near the grain boundaries. Figure 13 is also an example of the precipitation delay in the area in which dislocations and twin boundaries are included. Now, it has to be checked the possibility that the denuded zones near the grain boundaries were formed due to the segregation of the solute elements. However, as described in the experimental results, the distribution of the solute elements was quite uniform and no distribution difference was detected between the inside of the β grains and the neighbor of the grain boundaries in the as 2-step solution treated specimen in which the distinct denuded zones 50 μ m in width appeared in aging. Furthermore, it is difficult to think that the non-equilibrium segregation extends to 50 μ m in width in an early stage of aging at such a low temperature as 300°C. Therefore, it is considered that the main reason for the formation of the denuded zones near the β grain boundaries is the lack of excessive vacancies. From the technological point of view, it is important to analyze the factors like quenched-in vacancies which affect the aged microstructures and the precipitation kinetics, because the control of those factors leads to the control of the materials properties and the aging time⁽¹²⁾.

The raising up of the diffusivity of the solute elements by excessive vacancies can be considered as one of the effects of the quenched-in vacancies which influence the precipitation and the age hardening behavior. In addition, it must be considered that the quenched-in vacancies play an important role in the formation of the nucleation sites of the precipitates, because the α phase precipitated extremely homogeneously in the specimens in which much amount of quenched-in vacancies are considered to be involved, i.e. the specimens quenched from high temperatures and/or having a small density of the vacancy sinks (Figs. 5(b), 7-9). Since the details of such homogeneous precipitation is discussed in another report⁽¹⁰⁾, the effects of the factors which determine the amount of quenched-in vacancies, such as the vacancy sinks and the quenching temperatures, on the aging response are discussed next.

2. Effect of the vacancy sinks on aging response

Since both of the quenching temperatures in the 2-step solution treated specimen and the 800°C 1-step solution treated one are the same 800°C and they have the different β grain size, the effect of the β grain size on the aging response can be examined by comparing the experimental results in those two specimens. As described in the experimental results, the remarkably rapid precipitation of the α phase and the age hardening were observed inside the β grains in the 2-step solution treated specimen. On the other hand, the precipitation and the age hardening were delayed in the 800°C 1-step solution treated specimen and in the area near the grain boundaries in the 2-step solution treated specimen (Figs. 5(a), 9 and 10). If the denuded zones near the grain boundaries are regarded as the area where little amount of excessive vacancies are included, which situation can be caused during quenching by the annihilation of the majority of the vacancies existing at the quenching temperature of 800°C under the equilibrium condition, it can be considered that the width of about 50 μm of the denuded zones in the 2-step solution treated and 300°C, 64 h aged specimen (Fig. 3(c)) indicates that much amount of excessive vacancies within about 25 μm from the grain boundaries were absorbed to the grain boundaries during quenching from 800°C. Meanwhile, the grain size of the 800°C 1-step solution treated specimen is about 40 μm , which is almost the same as the width of the denuded zones in the 2-step solution treated specimen. Therefore, it can be considered that in the 800°C 1-step solution treated specimen, most of the vacancies existing at 800°C were annihilated to the grain boundaries during quenching and that the equilibrium concentration of vacancies at the aging temperatures were attained at least in an early stage of aging. On the other hand, it can be considered that the high concentration of vacancies which is close to the equilibrium concentration at 800°C are included inside the β grains in the as 2-step solution treated specimen. Similarly, the difference of the age hardening shown in Fig. 10 can be explained as the effect of the concentration difference of the excessive vacancies caused by the presence of the grain boundaries acting as the vacancy sinks.

The age hardening delay was also observed in the 3-step solution treated specimen, which had a relatively high density of dislocations (Fig. 12). Since the grain size of the 3-step solution treated specimen is equal to the 1200°C 1-step or 2-step solution treated one, it is considered that the age hardening delay is caused by a stronger effect of a small amount of excessive vacancies as a result of the role of dislocations as vacancy sinks and the low quenching temperature, rather than the effect of dislocations as the precipitation sites.

3. Effect of quenching temperatures on aging response

Since it is assumed that the 2-step and 1200°C 1-step solution treated specimens have almost the same β grain

sizes and show little differences in dislocation density as well as in density of vacancy sinks, the effect of the quenching temperatures (800 and 1200°C) on the aging response can be examined by comparing the aging response in both materials. As described before, it is reasonable to think that the concentration of excessive vacancies contained in the inside of the β grains in the 2-step solution treated specimen is close to the equilibrium concentration at 800°C and that the inside of the β grains in the 1200°C 1-step solution treated specimen has the concentration of quenched-in vacancies close to the equilibrium one at 1200°C. Hence, the difference of the age hardening behaviors at 300°C shown in Fig. 10 is considered to reflect the concentration difference of the quenched-in vacancies in both specimens. As described in the experimental results, the expanded denuded zones were observed near the grain boundaries in the 2-step solution treated and 300°C aged specimen (Fig. 9(b) and (c)), while the distinct denuded zones were not observed in the 1200°C 1-step solution treated and 300°C aged specimen (Fig. 5(b)). The difference can be explained as follows. In the 1200°C 1-step solution treated specimen, the β grain boundaries also act as the vacancy sinks of the excessive vacancies during quenching or in an early stage of aging. However, the equilibrium concentration of vacancies at 1200°C is exponentially higher than that at 800°C. So it is possible for a sufficient amount of vacancies to be supplied from the interior of the β grains to the vicinity of the β grain boundaries in which the vacancy concentration has been reduced. As a result, the more homogeneous precipitation without a distinct denuded zone occurred. Such a kind of phenomenon was also observed in the specimens aged at 500°C after the 1-step solution treatment: the denuded zones were formed more easily in the specimen quenched from 1000°C than in the specimen quenched from 1200°C (Figs. 7 and 8). The reason for this is as follows. The equilibrium concentration of vacancies at the quenching temperatures was not so high in the 1000°C solution treated specimen as in the 1200°C solution treated one. Consequently, the amount of vacancies enough to suppress the formation of the denuded zones was not supplied from the inside of the β grains to the vicinity of the β grain boundaries in the 1000°C solution treated specimen.

V. Conclusion

An effect of the solutioning conditions on the aging response in a β type titanium alloy, Ti-15V-3Cr-3Sn-3Al, was investigated. The obtained results are as follows.

(1) In the specimen quenched from higher temperatures in the β region or the one having a large β grain size and low dislocation density, the precipitations of the ω ($\leq 250^\circ\text{C}$) and the α ($\geq 300^\circ\text{C}$) phases and the age hardening are greatly accelerated at the aging temperatures lower than 350°C. For example, in the specimen water quenched from 1300°C, the age hardening begins only in 16 h at 200°C. At the aging temperatures from

300 to 500°C, The α precipitation is considerably homogeneous.

(2) In the above mentioned specimens, the precipitation delays and the denuded zones are sometimes observed near the β grain boundaries and the deformation twins, and in the area in which dislocations are introduced by the weak plastic deformation.

(3) In the specimens having a small grain size or slightly higher density of dislocations and quenched from lower temperatures in the β region, the precipitation and the age hardening are delayed, and the precipitation is heterogeneous.

(4) As described above, the solutioning conditions strongly influence on the aging response, and the phenomenon is closely related to the quenched-in vacancies of which concentration is determined by the quenching temperatures and the density of vacancy sinks such as β grain boundaries, dislocations, twin boundaries.

Acknowledgment

The authors would like to express their thanks to Prof. Dr. Jin-ichi Takamura, emeritus professor of Kyoto Uni-

versity, and Dr. Masao Kikuchi, Nippon Steel Corporation for the useful discussions and the instructions.

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