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Precipitation behavior in V–6W–4Ti, V–4Ti and V–4Cr–4Ti alloys

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Abstract

The cold rolled V–6W–4Ti, V–4Ti and V–4Cr–4Ti alloys were annealed at 900 and 1100 °C for recrystallization and solid solution, respectively. Large precipitates were found in the 900 °C annealed ones with main difference in the number density among the alloys. Followed the heat treatments, the alloys were annealed again at 400–900 °C for 1 h or aged at 600–800 °C for durations up to 50 h. Precipitation hardening was found in solid solution treated alloys after the annealing below 900 °C and after the aging at 600 °C. The precipitates are Ti and C-rich ones, without the enrichment of W in the V–6W–4Ti alloy. Results showed that the growth of the precipitates was controlled by the diffusion of interstitial solutes of C, N and O. V–4Cr–4Ti showed much stronger precipitation hardening than the others due to Cr addition.

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1. Introduction

It is well known that interstitial impurities in a vanadium alloy will strongly affect its mechanical performances [1–5]. Precipitation could remove interstitial impurities from the BCC solid solution, decreasing the effects. The formation of globular-shaped Ti-oxycabonitride in the thermomechanical processing brings about the shift of DBTT of a V–4Cr–4Ti alloy to lower temperature [3,5,6]. But fine precipitates formed in 700 °C annealing could strengthen the alloy and lower its ductility [3]. Moreover, interstitial impurities are the main cause for the formation of ultra-fine precipitates in the alloy during neutron irradiation at ~300–400 °C, which harden the alloy a lot and decrease the uniform elongation to less than 1% [7,8]. These results suggest that the precipitation behavior should be fully understood regarding its significance to the properties of the alloy. In recent years, some studies have been reported and showed that the effects of N and O on the precipitation were quite different [9,10]. It gives a possibility to control the precipitation and its hardening by controlling the concentration of each interstitial impurity. However, no report concerns the effect of the substitutional alloying elements on the behavior.

To understand the effects of the alloying elements, some new alloys were prepared in addition to

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V–4Cr–4Ti. The alloys were V–6W–4Ti and V–4Ti. Followed two kinds of pre-heat treatment of full recrystallization and solid solution annealing, the alloys were annealed or aged again. Precipitation behavior and the induced hardening were studied by hardness measurement and transmission electron microscope (TEM) observation. The present paper shows the results and the role of alloying elements to the precipitation.

2. Experimental procedure

Alloys were melted in a magnetic floating furnace. Detailed process for the preparation was reported in Ref. [11]. Canned alloy plates were hot rolled at 800 °C in air and took a vacuum annealing at 850 °C for 1 h afterwards, followed by a cold rolling to 1 mm thick with ~50% reduction in thickness. Some small pieces were further cold rolled to 0.25 mm thick for the preparation of TEM disks. The V–4Cr–4Ti alloy produced in Japan (heat #: NIFS-Heat-2) was also used in the present aging experiment. Its fabrication process could be found in Ref. [12]. Table 1 listed the chemical compositions of the plates and the interstitial impurity concentrations.

The as-rolled alloys were annealed at 900 °C for full recrystallization (Recrystallization Annealing – RA) or at 1100 °C for solid solution (Solid-solution Annealing – SA) treatment. Both treatments were conducted for 1 h in a vacuum less than 1×10^{-6} Torr. The 1 mm thick plates were then cut into small samples in dimensions of 5×10 mm^2 for hardness testing and TEM disks were punched out from the 0.25 mm thick foils. After mechanical grinding and electro-polishing, hardness samples along with the TEM disks were wrapped with Zr foils and isochronally annealed again at 400–900 °C for 1 h in the same vacuum condition. Instead of the annealing, some of them were aged at 600–800° for durations up to 50 h. Vicker's hardness (Hv) test was followed with a load of 0.5 kg and duration of 30 s. The microstructure of the alloys was then observed using the disks in a 200 keV transmission electron microscope.

3. Experimental results

3.1. Hardness change after the isochronally annealing

The as-rolled alloys showed different hardness after either 1100 °C annealing (SA) or 900 °C annealing (RA) for 1 h. The hardness data is listed in Table 2. It shows that V–6W–4Ti and V–4Cr–4Ti have similar hardness but both are harder than V–4Ti. Grain sizes of the alloys are also shown in the table. Evidently V–4Ti has larger grain size, which is decreased by W or Cr addition. As a result, the hardness of the alloy increased. However, the small change of the grain size is not so significant to change the hardness so much. Solid solution hardening by W or Cr should be the main contributor to the hardness increase.

Fig. 1 shows the change of the hardness after the 1 h isochronally annealing from 400 to 800 or 900 °C. For SA alloys, there was hardening at almost any temperature below 900 °C (see Fig. 1(a)). A hardening peak appeared at a critical temperature (CT) above which the hardening gets weaker. The CT for both V–4Ti and V–6W–4Ti is about 600 °C, but 700 °C for V–4Cr–4Ti, about 100 °C higher than that for the former alloys. Furthermore, the V–4Cr–4Ti alloy has much stronger hardening at the critical temperature than V–4Ti and V–6W–4Ti. Invariably, slight softening happened for all of the alloys at 900 °C. On the other hand, the RA

Table 1
Chemical compositions of the V-base alloys

Alloy	Alloying elements (mass%)			Impurities (wppm)		
	W	Ti	Cr	C	N	O
V–4Ti	–	3.99	–	120	30	280
NIFS-Heat-2	–	3.98	4.02	69	122	148
V–6W–4Ti	5.64	4.12	<0.05	50	4	350
V–4Cr–4Ti	–	4.19	4.18	60	3	350

Table 2
The hardness and mean grain size of the as-rolled alloys after 900 °C or 1100 °C annealing for 1 h

Annealing temperature (°C)	Vicker's hardness (Hv)			Mean grain size (μm)		
	V–4Ti	V–4Cr–4Ti	V–6W–4Ti	V–4Ti	V–4Cr–4Ti	V–6W–4Ti
900	106.2	127.6	131.0	22.6	17.6	16.6
1100	110.6	145.6	145.4	44.0	39.3	37.4

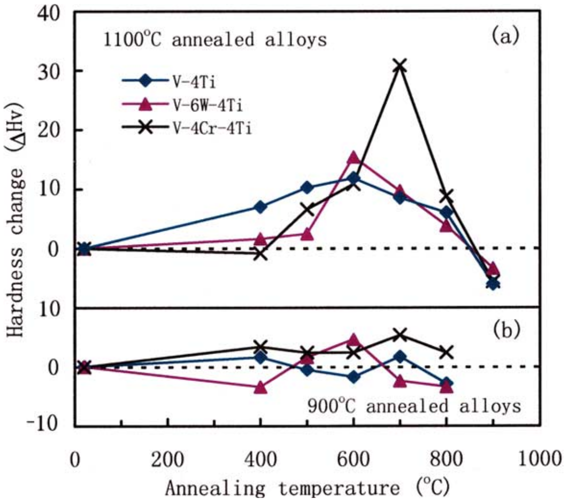

Fig. 1. Hardness change as a function of annealing temperature for (a) the 1100 °C annealed alloys and (b) the 900 °C annealed alloys.

alloys exhibited much small hardness change over the annealing temperatures, irrespective of the alloys (see Fig. 1(b)). There was always small hardening in the temperature range for V–4Cr–4Ti. For others, slight hardening happened at selective temperatures.

3.2. Hardness change after long time aging

The results are shown in Fig. 2. V–6W–4Ti was aged at 600–800 °C for 50 h, as that shown in Fig. 2(a). Similar to the 1 h isochronally annealing, the V–6W–4Ti in RA state showed small hardness change after the aging, with the difference of being softening at any of the temperature. Nevertheless, the change for the one in SA state is quite different from the isochronally annealing results, though likely some similarity in the trend of the temperature dependence. The difference is that the hardness decreased drastically with the increase of the aging temperature. In spite of much stronger hardening at 600 °C, softening appeared at and above 700 °C.

Fig. 2(b) shows the hardening at 600 °C, with the elapse of aging time for the alloys in SA state. It indicates that the hardening gets saturated after 10–20 h for V–6W–4Ti. It looks like that the V–4Cr–4Ti alloy would have behaved similarly. The hardness increment is likely to start to decrease after 20 h aging. However, the NIFS Heat V–4Cr–4Ti is somehow different from the other two alloys. Its hardness kept increasing at least for aging time up to 30 h. No matter how the difference of the time dependence is, both the V–4Cr–4Ti alloy and the NIFS heat have much higher aging-hardening capacity than the V–6W–4Ti alloy. The hardness increment for the former alloys is about twice as large as that for the latter one. But initially, the V–6W–4Ti alloy has high hardness increment after 1 h aging.

3.3. Precipitation in the alloys

3.3.1. Precipitates in the RA treated alloy

Two kinds of precipitates, large and fine ones, were found in the TEM observation. The as-rolled alloy showed many large precipitates with few dislocations after 900 °C-annealing for 1 h (see Fig. 3). The size of the precipitates is in the range from several tens nm to about 200 nm in diameter. Undergoing the same thermomechanical processing and heat treatment, V–6W–4Ti showed much more precipitates than V–4Cr–4Ti. The area number density for them is about $2.05 \times 10^{13}/\mathrm{m}^2$ and $8.47 \times 10^{12}/\mathrm{m}^2$, respectively. The precipitates in the NIFS heat look even less, perhaps due to its lower impurity concentration. Fig. 3(d) shows the precipitates in the V–6W–4Ti alloy after 50 h aging at 600 °C. In comparison with those precipitates in the alloy without aging, it could be deduced that no new precipitates were formed during the aging. But a little coarsening and reduction in number density of the precipitates seemed

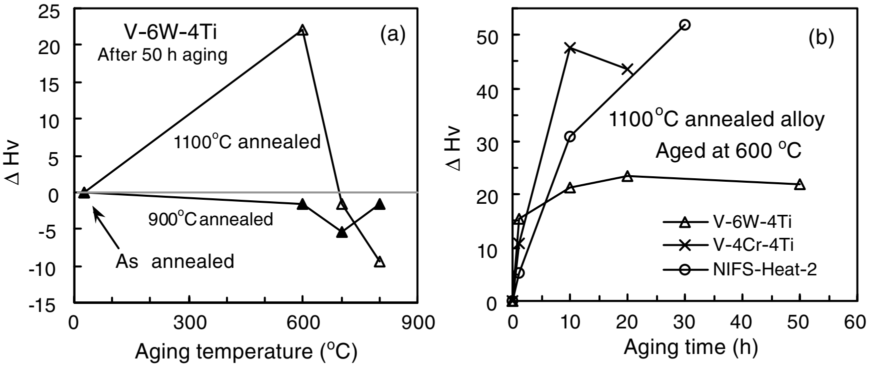

Fig. 2. The hardness change (ΔHv) after aging showing (a) temperature and (b) time dependence.

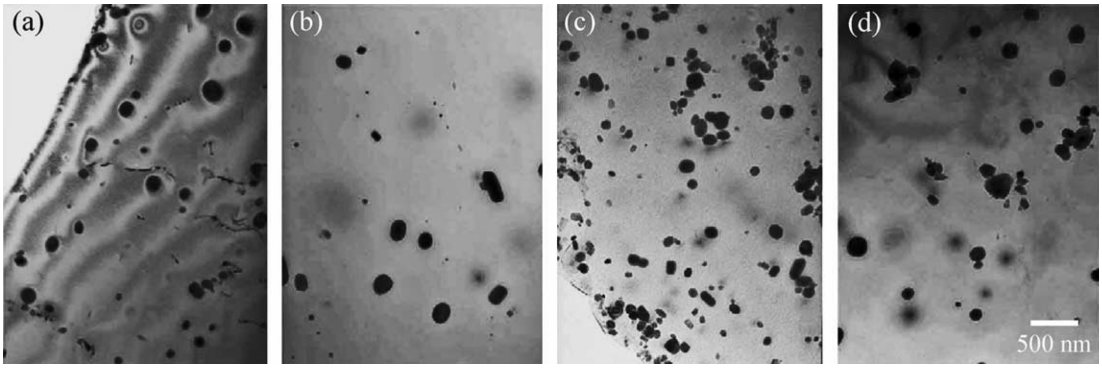

Fig. 3. TEM photos showing the precipitates, (a) V–4Cr–4Ti, 900 °C/1 h; (b) NIFS-Heat-2, 900 °C/1 h; (c) V–6W–4Ti, 900 °C/1 h; (d) V–6W–4Ti, 900 °C/1 h + 600 °C/50 h.

to have occurred. It accounts for the slight softening of the alloy after the aging.

TEM-EDX analysis results shown in Fig. 4(a) indicate that the precipitates contain very higher concentration of Ti and C, but much lower V than the matrix. As the peak of O and N was overlapped with the peak of V around 0.5 keV, their concentration cannot be determined from the pattern. Obviously, no W enrichment existed in the precipitate. Therefore, W in the alloy might have no effect on the precipitation behavior.

3.3.2. Precipitates in the SA treated V–6W–4Ti alloy

Fig. 5 is the TEM photos showing the precipitates in the SA treated V–6W–4Ti alloy after annealing from 400 to 900 °C for 1 h, together with the photo of the 600 °C-aged one. The hardness data is also shown in the figure. Originally, there is no precipitate in the alloy (see Fig. 5(7)). And yet, precipitation did not occur at 500 and 900 °C (see Figs. 5(1) and (6)), where the hardness is hardly changed. At 600 °C, fine precipitates in size of ∼2 nm appeared with high number density, corresponding to the strongest hardening in the temperature range. The precipitates get coarser with increasing temperature from 600 to 800 °C, while the number density decreased, corresponding to the decrease of the hardness. Fig. 6(a) shows the temperature dependence of the size and the number density of the fine precipitates. At 700 °C, in addition to the fine precipitates, some larger ones appeared and grouped in some micro-regions (Fig. 5(3)), which were not included in Fig. 6. TEM-EDX analysis result of the grouped precipitates is shown in Fig. 4(b). Not fully similar to the large precipitate observed in the RA treated alloy (see Fig. 4(a)), the precipitates contain not only high concentration of Ti and C but also high concentration of V. At 800 °C, the precipitates were plate-shaped with the diameter of ∼31.4 nm on average. These precipitates preferentially orientated to the ⟨100⟩ directions. The 50-h aged sample also contains high number density of very fine precipitates (Fig. 5(8)).

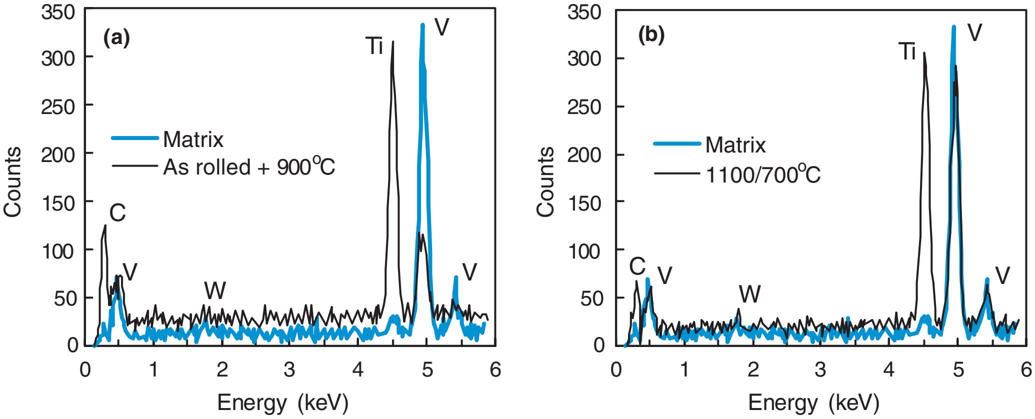

Fig. 4. TEM-EDX spectra of the matrix and the precipitate in the as-rolled V–6W–4Ti alloy after annealing at (a) 900 °C for 1 h and (b) 1100 °C for 1 h plus 700 °C for 1 h.

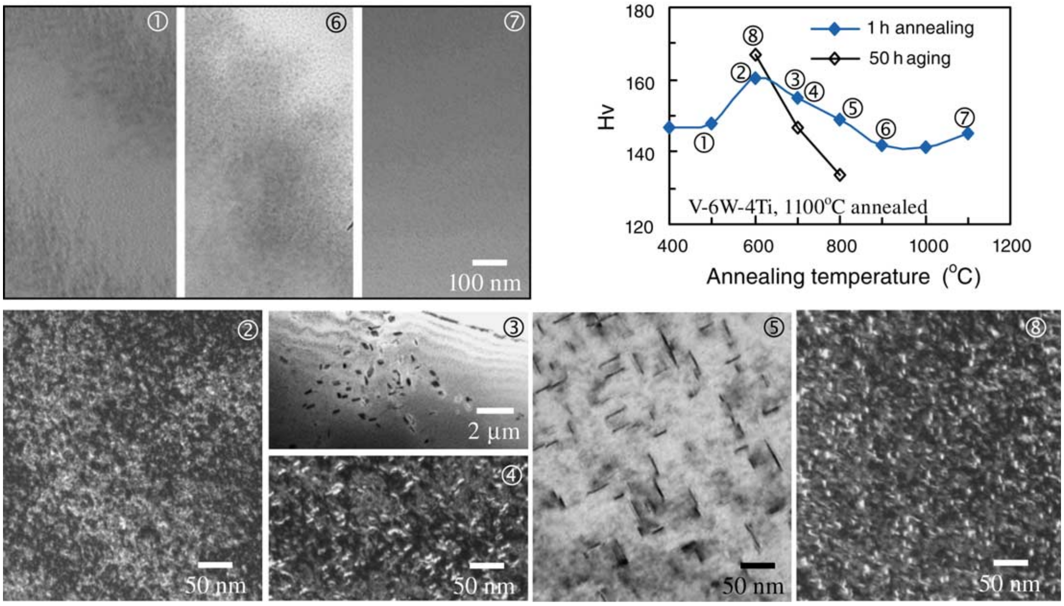

Fig. 5. Hardness (Hv) and microstructure at different annealing or aging temperature for the solid solution treated V–6W–4Ti alloys.

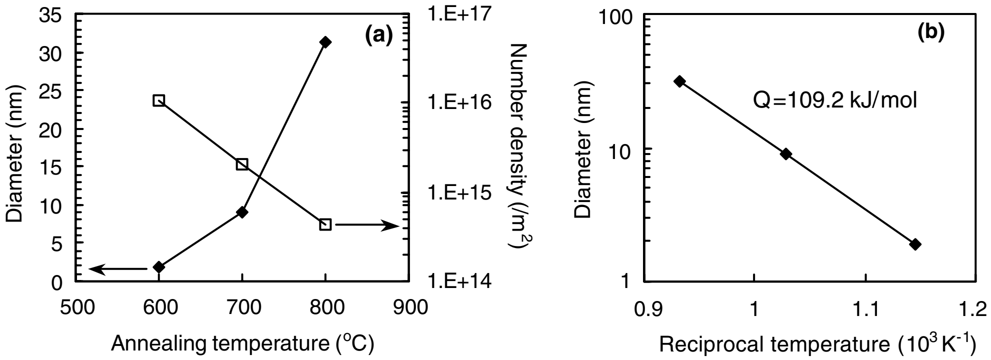

Fig. 6. The temperature dependence of (a) the diameter and number density of the fine precipitates appeared in the SA treated V–6W–4Ti alloy, (b) that showing the relationship between the diameter and the reciprocal temperature for activation energy evaluation.

4. Discussions

Many studies showed that precipitates in V–4Cr–4Ti alloy were Ti-rich and most likely to be Ti- (O, N, C) [12–15]. Usually two kinds of precipitates were observed, large and fine ones. The large globular-shaped precipitates may be formed during the hot-working process [12]. The fine one was usually thought to be formed during the heat treatment at ~700 °C [14]. In the present study, the 1100 °C solid solution treated V–6W–4Ti alloy and the additional 900 °C annealed one did not show any precipitates. It indicates that 900 °C annealing could not produce any precipitates in the alloy. Therefore, the large precipitates appeared in the RA treated alloys should be produced in the previous melting, hot-working and heating process. It seemed that precipitation in the V–6W–4Ti alloy was easier to take place than that in the V–4Cr–4Ti alloy during the process, since there were more precipitates in the former alloy even though both alloys had experienced the same thermo-mechanical processing. The precipitates are found Ti, C-rich and were presumed to be Ti- (O, N, C) precipitates also. The concentration of interstitial C, N and O in the matrix of the RA treated alloy must be very low due to the pre-existed large precipitates. As a result, precipitation would not occur anymore and hardening could not occur or is very small in the further annealing or aging as that shown in Fig. 1(b).

Precipitate hardening by fine precipitate is the main contributor to the hardness increase of the SA treated alloys during the annealing at 600–800 °C and the aging at 600 °C. This could be deduced from the good accordance of the hardness change with the characteristic of the fine precipitate shown in Fig. 5. However, precipitation would result in the loss of solid solution hardening because of the reduction of the interstitial solute and Ti in solution. As the fine precipitate grows bigger and bigger at temperature higher than the critical temperature with increasing time, the hardness of the alloys decreased due to the weakening of precipitation hardening and the loss of the solid solution hardening. The precipitate hardening could not counterbalance the loss of the solid solution hardening for the 50 h aging at 700 and 800 °C, resulting in the softening of the V–6W–4Ti alloy.

For the V–6W–4Ti alloy in solid solution, fine precipitates appeared at 600 °C and became larger with increasing temperature in the isochronally annealing. The incubation time for the nucleation of the precipitates is not known in the experiment. As the temperature is high, the time is presumed to be very short and is negligible as compared to the 1 h annealing. So the size of the precipitates could approximately be taken as their growth rate (V) in unit of nm/h. V could be expressed as: $V = V_0 e^{-\frac{Q}{RT}}$. Here V_0 is a pre-exponential term, Q is the activation energy of the growth, R is a gas constant and T is absolute temperature. Fig. 6(b) is the experimental data showing the relationship, from which the activation energy was evaluated to be about 109.2 kJ/mol. It is a little lower than the energy of oxygen diffusion in V and V–4Cr–4Ti, which are 123 and 130 kJ/mol, respectively [16]. However, precipitate growth contains the motion of Ti, C and N besides the motion of O. The activation energy for Ti diffusion must be much higher as compared to the O diffusion since Ti is substitutional solute. But its effect on the growth should be smaller as compared to the others due to its higher concentration in the alloy. Accordingly, the growth of the fine precipitates is likely to be controlled by the diffusion of the C, N and O interstitial solutes. C is commonly thought to be more mobile than O at elevated temperature [17]. It might be the cause that the activation energy of the precipitate growth is lower than the oxygen diffusion energy.

The results showed that the peak annealing hardening of the V–4Cr–4Ti alloy appeared at higher temperature than that of the V–6W–4Ti alloy in SA state. N.J. Heo studied another V–4Cr–4Ti alloy and found that high number density of fine precipitates occurred at 700 °C [9]. The precipitates exhibited a similar growth feature to those observed in the V–6W–4Ti alloy with increasing temperature. The hardening is also a precipitate hardening. Besides, V–4Cr–4Ti alloy showed a much stronger hardening than the V–6W–4Ti alloy both in the annealing and in the 600 °C aging. It suggests that the fine precipitates produced in V–4Cr–4Ti must be smaller and in higher number density than those in V–6W–4Ti. On the other hand, the annealing induced hardening of the V–6W–4Ti is quite similar to that of the V–4Ti alloy. It indicates that the difference between V–6W–4Ti and V–4Cr–4Ti is caused by Cr other than W in solid solution. Ti and Cr could form an intermetallic phase of $TiCr_2$ in the Ti–Cr binary system [18]. It is possible that there is a strong interaction between Cr and Ti in V–Cr–Ti system, which influences the nucleation and growth of the precipitates. Further investigation for the interaction is required.

5. Conclusions

The precipitation behavior in V–6W–4Ti was studied in detail, together with the precipitation hardening in the alloy and in other two alloys of V–4Cr–4Ti and V–4Ti. Just similar to that reported for the V–4Cr–4Ti alloy, the precipitates formed in the V–6W–4Ti alloy during annealing and aging are Ti and C-rich ones. The precipitates got coarsening with increasing annealing temperature started from ~600 °C, leading to the decrease of the precipitation hardening. The growth of the precipitates obeys to thermal activation kinetics with the activation energy of ~109.2 kJ/mol and thus is presumably controlled by the diffusion of C, N and O interstitial solutes in the alloy.

Precipitation only occurred in the solid solution treated alloy. When large precipitates formed in the working and heating history are not dissolved into the matrix during an annealing treatment, there would be no precipitation and hardening in the following annealing or aging.

Precipitation hardening in V–4Cr–4Ti is much stronger than that in V–6W–4Ti and V–4Ti. Cr addition is the main contributor to the strong hardening. One possible reason is that Cr-Ti atom interaction changed the precipitation behavior.

Tungsten (W) addition has no effect on the precipitation behavior of the V–4Ti alloy.

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