Martensitic Transformation Induced in Ti-15V-7Al Alloy at Low and High Temperatures^{*1}

Yoshito Takemoto¹, Miyu Tsunekawa^{1,*2}, Yuji Manabe^{2,*3}, Soushi Itano^{2,*3} and Yuji Muraoka³

¹Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan

²Faculty of Engineering, Okayama University, Okayama 700-8530, Japan

³Research Institute for Interdisciplinary Science, Okayama University, Okayama 700-8530, Japan

Ti-15V-7Al alloy, which has a composition exhibiting peculiar phenomena upon tempering, was prepared and its martensitic transformation behavior during cooling and heating was investigated. The structure of the quenched specimen mostly consisted of the β -phase and a small quantity of α'' martensite near the grain boundaries. When heating an elastically bent strip of the specimen, spontaneous bending occurred, as reported for some other alloys. Subzero treatment using LN₂ newly induced some martensites around the prior martensites formed by quenching, but no martensites were formed in the single β region. The formation of the martensites by the subzero treatment exhibited time dependence. Even tempering at 550°C for 3 s, induced the formation of coarse martensites throughout the specimen. All martensites formed by the quenching, the subzero treatment or the tempering disappeared completely upon heat treatment at 200°C for 300 s, resulting in a single β -phase. However, the coarse martensites were regenerated from the single β -phase by tempering at 550°C for a short time, which means that the martensite behavior in the range of 200–550°C is reversible. Continuous isothermal aging at 550°C led to marked hardening through the process $\beta \rightarrow \text{coarse } \alpha'' \rightarrow \text{fine } \alpha'' \rightarrow \beta + \text{fine } \alpha$. Both an M_s curve and a free-energy model, which can explain the martensite formation at low and high temperatures and the annihilation at 200°C, are proposed. [doi:10.2320/matertrans.M2018185]

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1. Introduction

β (bcc) type titanium alloy is well known to exhibit metastable phase with crystallographic structures α' (hcp), α'' (ortho.) or ω (trig.), depending on the chemical composition of the bcc matrix.^{1,2)} The α' and α'' martensites can be easily observed with an optical microscope, but the ω -phase cannot be observed without transmission electron microscopy (TEM) because of its small size. These metastable phases influence not only the mechanical properties but also the functions of twin-induced plasticity (TWIP),^{3,4)} low Young's modulus,⁵⁾ super-elasticity and shape memory.⁶⁾ Although the characteristics of β titanium alloys are usually classified using the Mo equivalence,⁷⁾ the value of Bo-Md⁸⁾ or the electron valence $\Delta e/a$,⁹⁾ these methods have not been successfully applied to the β alloys containing a significant amount of aluminum.^{10–13)} If 7 mass% aluminum, which is a strong α stabilizer, is added to the β alloys with a lower limit of the composition, the β -phase is stabilized and retained after quenching. When such alloys are tempered at 400–500°C for a short time, α'' martensite is formed, resulting in marked hardening. Moreover, a strip of the quenched alloy subjected to elastic bending will deform spontaneously in the bending direction upon heating to 420°C. When a quenched strip of some alloys is bent into a U-shape and heated, shape recovery occurs before the spontaneous bending. One of the authors has reported that such peculiar phenomena occur in Ti-(4Fe, 10Mo, 35Nb)-7Al alloys^{10–13)} (respectively referred to as 4FeA, 10MoA and 35NbA hereafter). However, many unsolved problems related to the essential behavior of the

$\beta \rightarrow \alpha''$ transformation remain. Will the residual β -phase after quenching be transformed to the α'' martensite by subsequent subzero treatment? Although the quenched α'' martensite disappears at 200°C and becomes the β -phase, why is the α'' martensite regenerated at a much higher temperature?

In this study, Ti-15V-7Al alloy, which has a composition condition that exhibits the above peculiar phenomena,^{10–13)} was investigated to clarify the overall picture of the martensite transformation under various heat treatments.

2. Experimental Procedure

Table 1 shows the chemical composition of the Ti-15V-7Al alloy (referred to as 15VA hereafter) used in this study. All compositions in this paper are given in mass%. The oxygen content is slightly less than that in common titanium alloys. Plates with 3.5 mm thickness were cut from an ingot of the alloy and polished mechanically then heated at 1050°C for 1.8 ks under a vacuum as a solution treatment (ST), which was followed by quenching in iced water (STQ). To confirm that the above peculiar phenomena occur upon heating, a thin strip of the alloy bent elastically using a jig was heated to 420°C on a hot plate at a heating rate of 0.4°C/s, during which the shape was recorded at intervals of 10°C. A salt bath maintained at a high temperature was used for a tempering treatment. A subzero treatment was also carried out using liquid nitrogen (LN₂). Vickers hardness

Table 1 Chemical composition of 15VA alloy.

(mass%)				
Elements	V	Al	O	Ti
mass%	14.7	7.2	0.083	Bal.

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^{*2}Graduate Student, Okayama University

^{*3}Undergraduate Student, Okayama University

Fig. 1 Shape evolution during heating of the bent elastic strip of 15VA.

was measured at 15 points with a load of 2.94 N, and the average Vickers hardness at 13 points was adopted, with the maximum and minimum values excluded. Optical micrographs of samples were taken at identical positions before and after the heat treatment, where the samples were prepared by chemical etching after a small amount of polishing and electropolishing. The electropolishing was performed in a solution of methanol, butanol and perchloric acid (volume fraction 10:6:1) at -40°C . The etchant used was composed of fluoride acid, nitric acid and water (1:1:2–10). X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM) were used to analyze the microstructure. The thin foils used for STEM observation were prepared by electropolishing or a focused ion beam (FIB) method.

3. Results and Discussion

3.1 Shape evolution and age-hardening behavior with heating

Figure 1 shows the shape evolution of the STQ strip slightly bent using a jig while heating to 420°C . The shape of the specimen slightly deformed at around 200°C , the end of the sample came away from the jig above 240°C , then the bending progressed spontaneously with increasing temperature. Although not shown in Fig. 1, the shape of the U-shaped sample exhibited a slight recovery at 70°C , then the bending progressed above 280°C . It was confirmed that 15VA also shows peculiar phenomena similar to those of 10MoA and 35NbA alloys. Figure 2 shows the hardening behavior during isothermal aging at several temperatures. The hardness of the STQ specimen was 280 Hv. Aging at 450°C resulted in the longest incubation period before the start of hardening, but the increase in hardness was the greatest. Above 450°C , slight softening was observed during short-time aging.

3.2 Martensite transformation with cooling

Figure 3 shows the microstructure before and after subzero treatment using LN_2 . Most of the STQ specimen consists of the β -phase, but a small amount of acicular α'' martensites can be seen near the grain boundaries as shown in Fig. 3(a). In some parts of the specimen, there was also a single β region with no α'' martensite even at the grain boundaries.

Fig. 2 Change in hardness with isothermal aging at 250 – 550°C .

Figure 3(b) shows a micrograph of the same area after the subzero treatment at LN_2 temperature for 900 s. The amount of α'' martensite clearly increased, which means that the α -phase is more stable at low temperatures than the β -phase. On the other hand, in the single β region in the STQ state, no α'' was formed by the subzero treatment. This suggests that the formation of subzero α'' requires certain preferential sites such as quenched α'' . Comparing Figs. 3(a) and (b), hardly any quenched α'' was grown by the subzero treatment and newly formed α'' was observed.

To clarify the subzero α'' formation process, the electroresistivity was dynamically measured during the subzero treatment. The specimen had a size of $6 \times 3 \times 0.2 \text{ mm}^3$ with four terminals at each end and a thermocouple at the center that were spot-welded. It was directly immersed into LN_2 for 352 s. The change in the electroresistivity is shown in Fig. 4. The specimen reached LN_2 temperature in 2 s, then the resistivity increased for 4 s, then dropped abruptly and remained constant without fluctuation. This result means that the formation of subzero α'' has a similar time dependence to that of an isothermal martensite. The increase in resistivity is related to the growth stage of fine ω or α'' embryos,¹⁴ and the abrupt decrease in electroresistivity is considered correspond to the formation of α'' martensites of micron size.

Fig. 3 Optical micrographs taken before (a) and after (b) subzero treatment.

Fig. 4 Change in electroresistivity during subzero treatment.

3.3 Martensite transformation and inverse transformation with heating

Figure 5 shows the microstructure before and after the tempering at 550°C for 3 s. Unexpectedly, a coarse acicular product formed in the entire sample in a very short time. For reference, a smaller quantity of the acicular product than that in (b) was also observed upon aging at 550°C, even for 1 s (not shown here). Although no subzero α'' was generated in the single β region as mentioned above, the tempering at 550°C produced the coarse acicular structure in spite of the difference in the initial structure. Figure 6 shows XRD profiles obtained before (a) and after (b) the tempering at 550°C for 3 s. The structure of the STQ sample (a) is almost β -phase, and small α'' peaks can be seen before the tempering, whose intensity became much stronger after the tempering (b). Therefore, the acicular product generated by tempering was also α'' .

Fig. 5 Optical micrographs taken before (a) and after (b) tempering at 550°C for 3 s.

Fig. 6 XRD profiles obtained before (a) and after (b) tempering at 550°C for 3 s.

Fig. 7 Microstructure evolution with thermal history. The photographs correspond to the letters indicated in the thermal history in (f).

Fig. 8 Microstructure evolution with isothermal aging at 550°C.

Figure 7 shows optical micrographs taken at the points indicated by letters a–e in the thermal history diagram shown in (f). Figure 7(a) shows the acicular α' martensite induced by the tempering at 550°C for 3 s, similar to that in Fig. 5(b). Figure 7(b) shows the structure after subzero treatment for 900 s using LN₂. Hardly any structural change from Fig. 7(a) to Fig. 7(b) can be observed, even though a little martensite may be generated. Figure 7(c) shows the inverse transformation to a single β -phase by aging at 200°C for 300 s. Figure 7(d) shows the structure after the second subzero treatment, where no martensite was observed at all. This is presumably due to the loss of the preferential sites as mentioned in section 3.2. However, α' martensite was induced again by the second tempering as shown in Fig. 7(e). As a result, it was found that the formation and annihilation of martensite can occur reversibly in a short time in the temperature range of 200–550°C.

3.4 Microstructure evolution with isothermal aging at 550°C

Figure 8 shows the microstructure evolution with increased isothermal aging at 550°C. Although the coarse acicular martensites were clearly observable up to aging for 60 s, they became obscure after 120 s and each grain became dark with increasing aging. Figure 9 shows XRD profiles obtained during isothermal aging at 550°C. After aging for 180 s, the hardness abruptly increased and the optical micrograph exhibited dark grains without coarse acicular martensites; however, the $\beta + \alpha'$ structure was still retained. The XRD profile obtained after aging for 900 s indicated $\beta + \alpha$ (or α') with no α'' peaks. Figure 10 shows STEM images and the corresponding vanadium maps after different durations of isothermal aging at 550°C. Because the coarse martensite structure formed during short-term aging is easily transformed to the β -phase by electropolishing, the TEM foils of

Fig. 9 Change in XRD profile with isothermal aging at 550°C.

Fig. 11 Schematic drawing of M_s (solid) and T_0 (dashed) curves used to explain the martensite transformation induced at low and high temperatures.

Fig. 10 STEM images and V element maps after isothermal aging at 550°C for (a) 7 s, (b) 60 s, (c) 180 s and (d) 900 s.

the specimens after aging for 7 s and 60 s were prepared by the FIB method. No compositional distribution was detected in the specimens aged for 7 s and 60 s. However, a very fine acicular product was observed in the sample aged for 180 s, and the vanadium content in the product was low. Considering the results of XRD, the fine product is an orthorhombic α'' structure with a low vanadium content owing to atomic diffusion. Note that an orthorhombic structure is called α'' irrespective of the compositional fluctuation. The acicular product formed after aging for 900 s (Fig. 10(d)) also contains dilute vanadium, but it is α -phase according to the XRD results. The isothermal aging at 550°C induces the following process: $\beta \rightarrow$ coarse α'' (martensitic transformation) $\rightarrow$ fine α'' (diffusion) $\rightarrow \beta +$ fine α (diffusion).

3.5 Martensite transformation at low and high temperatures

One of the authors previously proposed a bow-curved M_s model to explain the martensite formation under high-temperature tempering.¹²⁾ However, the formation of

martensite at both LN_2 temperature and 550°C in the present study cannot be explained using the model. Figure 11 shows the newly modified M_s curve used to explain the present results. The dashed curve T_0 denotes the temperature at which the Gibbs free energies of the α and β phases are equal. Since a small quantity of martensite is introduced by the STQ, the composition of 15VA should be located within the nose of the M_s curve at a high temperature. However, only a limited amount of the martensite can grow during quenching owing to the time dependence of the martensite formation. Accordingly, the formation of the martensite is restricted to at the grain boundaries, which act efficiently as heterogeneous nucleation sites. For reference, the time required for quenching from 1050°C to 0°C was measured to be only 0.2 s.

The subzero treatment only produced new α'' martensite in the vicinity of the quenched α'' because the LN_2 temperature is under the M_s curve. However, the fact that no subzero α'' was formed in the single β region may be related to the behavior of the shear stress with decreasing temperature peculiar to a bcc structure. It is well known that the critical

shear stress (CRSS) in a bcc structure rapidly increases with decreasing temperature.¹⁵⁾ Accordingly, the shear stress required for the martensite formation may also increase at low temperatures. The existence of quenched α'' provides the preferential sites for the formation of subzero α'' , but much more energy for nucleation will be required in a single β region. This is the reason why no subzero α'' was formed in the full β structure (Fig. 7(c)).

On the other hand, tempering at 550°C, within the nose of the M_s curve, even for 3 s, is sufficiently long to induce a normal martensite. The softening of the lattice at 550°C will also promote the growth of coarse martensite. The most inexplicable problem is that all the martensite was reversibly transformed to the β -phase by aging at 200°C. According to the experimental results, the stable phases alternately change between β and α in the order β (1050°C) $\rightarrow$ α (550°C) $\rightarrow$ β (200°C) $\rightarrow$ α (LN₂). Pure iron is well known to exhibit similar transformation behavior, δ (bcc) $\rightarrow$ γ (fcc) $\rightarrow$ α (bcc), caused by a magnetic transition¹⁶⁾ (paramagnetic $\rightarrow$ ferromagnetic). Unfortunately, 15VA including 10MoA and 35NbA does not undergo a ferromagnetic transition, so this discussion cannot be applied.

Figure 12 shows a schematic diagram of the free-energy (G) relation between β and α for different temperatures. It is assumed that G^α has a spinodal decomposition (SD)-type relation in the $\beta + \alpha$ field. In the $\beta + \alpha$ field, a maximum appears in G^α . With decreasing temperature, the position of the maximum G^α shifts to the higher-composition side. Assuming that the composition of 15VA is c_0 in the figure, the energy relation between both phases changes as follows: $G^\beta < G^\alpha$ (1050°C), $G^\alpha < G^\beta$ (550°C), $G^\beta < G^\alpha$ (200°C), and $G^\alpha < G^\beta$ (LN₂). This relation can successfully explain the peculiar phase stability. It is considered that the two minima of G^α correspond to α' and α'' . Generally, the composition range of α' is narrow and that of α'' is extensive, which also correspond to the change in the ratio of the lattice parameters

b/a of the orthorhombic α'' with the composition. Accordingly, the conceivable binodal line (solid) should be asymmetric. Davis *et al.*¹⁾ first reported the SD of β titanium alloy in the 1970's and recently Saeki *et al.*¹⁷⁾ also reported it in detail.

4. Conclusions

The martensite transformation behavior of 15VA alloy subjected to several heat treatments was investigated. The results can be summarized as follows:

- (1) The structure in the sample subjected to STQ consists of mainly β -phase with a little α'' only at grain boundaries. 15VA exhibited a peculiar shape evolution with heating as well as 4FeA, 10MoA and 35NbA alloys.
- (2) Subzero α'' was formed only in the vicinity of the quenched α'' , and it was not formed in the single β region. The martensite formation exhibited a time dependence.
- (3) Aging at 450°C exhibited the longest incubation period before the start of hardening, but the amount of hardening was the greatest. During short-time aging above 450°C, slight softening due to the formation of coarse martensite was observed.
- (4) Tempering at 550°C resulted in the introduction of coarse α'' martensites throughout the specimen, but they inversely transformed to a single β -phase upon aging at 200°C. The martensite transformation behavior was reversible in a short time in the range of 200–550°C.
- (5) Isothermal aging at 550°C induced the following process: $\beta \rightarrow$ coarse α'' (martensitic transformation) $\rightarrow$ fine α'' (diffusion) $\rightarrow$ $\beta +$ fine α (diffusion), resulting in marked hardening.
- (6) Both an M_s curve and a free-energy model, which can explain the martensite formation at low and high temperatures and the annihilation at 200°C, were proposed.

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REFERENCES

- 1) R. Davis, H.M. Flower and D.R.F. West: *J. Mater. Sci.* **14** (1979) 712–722.
- 2) M. Hida and E. Sakedai: *Bull. Inst. Metals* **26** (1987) 887–895.
- 3) Y. Takemoto, M. Hida and A. Sakakibara: *J. Japan Inst. Metals* **60** (1996) 1072–1078.
- 4) S. Hanada: *Bull. Inst. Metals* **25** (1986) 755–764.
- 5) Y. Takemoto, I. Shimizu, A. Sakakibara and T. Senuma: *J. Japan Inst. Metals* **70** (2006) 110–113.
- 6) H.Y. Kim, H. Hosoda and S. Miyazaki: *J. JILM* **55** (2005) 613–617.
- 7) E.W. Collings: *Materials Properties Handbook Titanium Alloys*, (ASM International, 1994) pp. 1–122.
- 8) M. Morinaga, J. Saito and M. Morishita: *J. JILM* **42** (1992) 614–621.
- 9) E. Ezaki, M. Morinaga, M. Kato and N. Yukawa: *Acta Metall. Mater.* **39** (1991) 1755–1761.

Fig. 12 Schematic diagram showing free energy (G) relation between α and β . The curve of G^α in the dual phase ($\alpha + \beta$) field shows a spinodal-decomposition-type relation. With decreasing temperature, the stable phase at the c_0 composition alternately changes. Possible binodal (solid) and spinodal (dashed) lines are also shown.

- 10) Y. Takemoto, K. Fujii, S. Nakatsuka and T. Senuma: *J. Japan Inst. Met. Mater.* **77** (2013) 368–374.
- 11) Y. Takemoto, M. Ochi, T. Senuma, J. Takada, I. Shimizu and K. Matsugi: *J. Japan Inst. Metals* **76** (2012) 449–455.
- 12) M. Ijiri, Y. Tomita, T. Ishikawa, K. Kadowaki and Y. Takemoto: *J. Japan Inst. Met. Mater.* **81** (2017) 345–351.
- 13) M. Ijiri and Y. Takemoto: *J. Japan Inst. Met. Mater.* **79** (2015) 468–473.
- 14) Y. Takemoto, T. Maruyama and M. Ijiri: *J. Japan Inst. Met. Mater.* **82** (2018) 256–261.
- 15) S. Takeuchi: *Bull. Inst. Metals* **7** (1968) 14–26.
- 16) T. Omori and R. Kainuma: *Materia Japan* **54** (2015) 398–404.
- 17) S. Saeki, S. Kobayashi and S. Okano: *J. Japan Inst. Met. Mater.* **82** (2018) 197–203.