**Heating-induced martensitic transformation and time dependent shape memory
behavior of Ti-Nb-O alloy**

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Abstract

Temperature dependence of nano-sized lattice modulation (nanodomains) which was introduced by oxygen atoms and martensitic transformation behavior of the (Ti-23Nb)-1.0O alloy were systematically investigated. Nanodomains in the β phase became unstable at higher temperatures and disappeared above 373 K, where time-dependent heating-induced forward transformation (HIFT) was confirmed in the (Ti-23Nb)-1.0O alloy. Thermally activated process of HIFT in the (Ti-23Nb)-1.0O alloy was the diffusion of oxygen atoms in nanodomains. Anomalous temperature dependence of shape memory behavior was also confirmed in the (Ti-23Nb)-1.0O alloy and its mechanism was successfully explained by the diffusion of oxygen atoms during tensile deformation.

Keywords: Martensitic transformation, Nanodomain, Titanium alloys, Shape memory effect,

Lattice modulation

1. Introduction

β -Ti alloys have received a lot of attention in recent years as new candidates for not only low Young's modulus materials but also biomedical Ni-free shape memory alloys (SMAs). To develop β -Ti SMAs many efforts have gone into elucidating the effect of alloying elements [1-19] and thermo-mechanical treatments [20-25] on the shape memory effect (SME) and superelasticity (SE). It has been reported that the addition of interstitial elements such as oxygen [4] and nitrogen [7, 15, 16, 19] is one of the most successful method to obtain superior SME and SE. However, there are ongoing discussions about the martensitic transformation behavior of β -Ti alloys with interstitial elements. It has been reported that the addition of oxygen atoms suppresses the martensitic transformation [4, 26] and decreases the martensitic transformation start temperature (M_s) significantly (-160 K / at.% O [4]), however, its detailed mechanism still remained to be clarified. On the other hand, the relationship between interstitial oxygen atoms and the martensitic transformation has been also subject to intense study of Gum metal (Ti-23Nb-2Zr-0.7Ta-1.2O (at.%)) [27-35]. Several unique properties such as non-linear elastic deformation, invar-like behavior and pseudoelasticity are confirmed in the Gum metal, and many researchers have pointed out that the stress-induced martensitic transformation and interstitial oxygen atoms play critical roles in the unique properties of Gum metal.

Recently, we reported anomalies in the microstructure and martensitic transformation behavior of the oxygen-added β -Ti alloy [35-38]. Diffuse scattering along $\langle 110 \rangle_{\beta}^*$ was confirmed in the selected area diffraction patterns (SADPs) which is due to the nanosized (< 3 nm) $\{110\}_{\beta} \langle 1\bar{1}0 \rangle_{\beta}$ transverse type lattice modulation (nanodomain) in the β phase. This lattice modulation occurs by the shuffling process involved in the β - α'' martensitic transformation. Taking into account the crystallographic symmetry of shuffling, nanodomains can be divided into six variants (the definition of each variant is shown in Table 1 of Ref. [37]), and all of them distributed equivalently and randomly in the parent β phase. It was suggested that the origin of nanodomains is the relaxation of local strain fields around randomly distributed oxygen atoms in octahedral sites by the shuffling of the martensitic transformation. Strain fields formed around oxygen atoms locally induce the martensite-like structure (i.e. nanodomains), however, the formation of long-range distribution to form the α'' martensite is suppressed because the shuffling modes of each variant is different each other. The mechanism of SE in β -Ti alloys with nanodomains is therefore deferent from that of the other normal SMAs such as Ti-Ni and oxygen-free β -Ti alloys which reveal the normal martensitic transformation.

Nanodomain structure in oxygen-added β -Ti alloys can explain the effect of oxygen addition on the martensitic transformation and unique properties of Gum metals, however,

following two points have to be considered carefully for the clear understanding of the phenomena: (1) temperature dependence of nanodomain stability and (2) diffusion of interstitial oxygen atoms in nanodomains. Nanodomains are introduced by the local shuffling which is a component of the martensitic transformation, thus the stability of nanodomain structure should be affected by specimen temperature similarly to the normal martensitic transformation. Positions of interstitial oxygen atoms also should have decisive influence on the distribution of the nanodomains and shape memory behavior of oxygen-added β -Ti alloys. Hence, in this study, the effect of temperature on the stability of nanodomain structure was investigated in the (Ti-23Nb)-1.0O alloy by TEM observation at various temperatures. The temperature dependence can be understood by considering the stability of α'' martensite in the binary Ti-23Nb alloy. Diffusion of oxygen atoms during the tensile deformation and resulting changes in the martensitic transformation and shape memory behavior were also investigated by tensile tests and in situ X-ray diffraction (XRD) measurements. Heating-induced forward martensitic transformation and time-dependent shape memory behavior were confirmed, and these unique phenomena can be successfully explained by the diffusion of oxygen atoms during tensile deformation.

2. Experimental

The alloy compositions of this study are Ti-23Nb and (Ti-23Nb)-1.0O (at.%) which are similar to our previous study [37]. The alloy ingots were fabricated by the Ar arc melting method using high purity Ti (99.9%), Nb (99.9%) and TiO₂ (99.9%). The oxygen content was controlled by the amount of TiO₂ powder. The ingots were homogenized at 1273 K for 7.2 ks in a vacuumed quartz tube and cold-rolled with a reduction of 98.5 % in thickness. Specimens for tensile tests, in situ XRD measurements and TEM observation were cut using an electro-discharge machine and the damaged surface was polished by chemical etching. Specimens for tensile tests and in situ XRD measurements were solution treated at 1173 K for 1.8 ks in an Ar atmosphere, followed by water quenching. In case of the specimen for TEM observation, the solution treatment was carried out at 1073 K for 0.6 ks so as to obtain a $\{001\}_{\beta}<110>_{\beta}$ deformation texture which was useful for TEM observation.

Tensile tests were carried out at 173 ~ 573 K and the gauge length of tensile tests was about 8 mm. Tensile direction of this study was parallel to the rolling direction which was almost equal to $<110>_{\beta}$ owing to a strong texture $\{112\}_{\beta}<110>_{\beta}$ formed by the thermo-mechanical treatment. Two types of tensile tests were carried out: (1) strain-temperature (S-T) curve mode (heating and cooling under a constant stress) (2) stress-strain (S-S) curve mode (loading and unloading under a constant temperature). Heating and cooling rate of S-T mode was $\pm 2 \sim 20$ K / min and a strain rate of S-S mode was 2.5×10^{-3}

$\sim 2.5 \times 10^{-5} \text{ s}^{-1}$. Before the tensile tests, each specimen was held at each testing temperature for 0.3 ks to keep the specimen temperature constant. In situ XRD measurements under the constant tensile stress of 200 MPa were carried out during heating from 333 K to 513 K. Heating rate of in situ XRD measurements was 12 K / min. Specimen temperature was kept constant during XRD measurements and measurement time at each temperature was about 0.3 ks. TEM specimen was prepared by a conventional twin-jet polishing method with a solution of hydrofluoric acid : sulfuric acid : methanol = 2 : 5 : 93 in volume at about 233 K. TEM observation was carried out at 90 ~ 423 K using JEOL 2010F instrument operated at 200 kV.

3. Results and discussions

3.1. Microstructure

Figure 1 shows selected area diffraction patterns (SADPs) of the (Ti-23Nb)-1.0O alloy at (a) 90 K, (b) 293 K (room temperature), (c) 353 K, (d) 373K and (e) 423 K. Zone axis of these SADPs was parallel to $[001]_{\beta}$ direction and all of SADPs were taken from the same region in the same grain. Intensity profiles along $[110]_{\beta}^*$ (between the diffraction spots of $0\bar{2}0_{\beta}$ and 200_{β}) and $[1\bar{1}0]_{\beta}^*$ (between the diffraction spots of $\bar{2}00_{\beta}$ and $0\bar{2}0_{\beta}$) are shown in Figs. 2(a) and 2(b), respectively. In the SADP obtained at 293 K (Fig. 1(b)), the diffuse streaks along $\langle 110 \rangle_{\beta}^*$ directions and the intensity maxima at 1/2 position of diffraction

spots were clearly confirmed. This is consistent with the previous report [37] and implies the presence of nanodomain structure at room temperature. By decreasing specimen temperature from 293 K to 90 K, the intensity of both two types of diffuse streaks ($[110]_{\beta}^*$ streaks and $[1\bar{1}0]_{\beta}^*$ streaks) increased. Unfortunately we could not obtain the dark field image of nanodomains at 90 K due to the specimen drift, however, the increase in the intensity of diffuse streaks means the growth of nanodomains by cooling. It is also noted that no α'' martensite was confirmed even at 90 K, implying that the martensitic transformation of the (Ti-23Nb)-1.0O alloy during cooling under zero stress was suppressed by the randomly distributed six variants of nanodomains. Suppression of martensitic transformation by oxygen addition was also observed by DSC measurements as shown in Fig. 3 [37]. On the other hand, the intensity of diffuse streaks along $\langle 110 \rangle_{\beta}^*$ decreased by heating from 293 K to 353 K, and became faint above 373 K. This means that the nanodomain structure became unstable with increasing specimen temperature and disappeared above 373 K.

The above temperature dependence of the nanodomain structure is explained by the stability of α'' martensite in the oxygen-free Ti-23Nb alloy. The nanodomain is formed by the nano-sized transverse type lattice modulation of $\{110\}_{\beta} \langle 1\bar{1}0 \rangle_{\beta}$ introduced by local strain fields around oxygen atoms [37], and this lattice modulation corresponds to the shuffling process of the β - α'' martensitic transformation. At low temperature, therefore, the local strain

fields around interstitial oxygen atoms were easily relaxed by the shuffling because the α'' martensite is stable at lower temperatures. On the other hand, the relaxation of local strain field by shuffling became difficult at higher temperatures, thus the nanodomain structure disappeared above 373 K. It is important to note that the temperature at which the nanodomain structure disappeared by heating approximately corresponds to the reverse transformation temperature of the Ti-23Nb alloy as shown in Fig. 3. Martensitic transformation and shape memory behavior were also affected by these changes of the nanodomain structure as described below.

3.2. Martensitic transformation

Procedures of S-T mode tensile tests of this study are shown in Fig. 4(a). At first, specimens were cooled down to 173 K without tensile stress, then tensile stress was applied at 173 K and heating / cooling thermal cycling (heating and cooling rate is ± 10 K / min) was carried out under a constant tensile stress. Figure 4(b) shows the S-T curves of the (Ti-23Nb)-1.0O alloy at a constant stress of 200 MPa. The inset of Fig. 4(b) shows a typical schematic S-T curve of normal shape memory alloys. Changes of S-T curve in normal shape memory alloys are explained as follows. When the tensile stress is applied to the specimen at a low temperature below M_s , the specimen is elongated due to the reorientation of martensite

variants. During heating under a constant stress, a decrease of tensile strain due to shape recovery by reverse transformation starts at A_s and finishes at A_f . On the other hand, during cooling an increase of tensile strain due to stress-induced martensitic transformation starts at M_s and finishes at M_f . In the (Ti-23Nb)-1.00 alloy, the cooling curve of the first cycle and heating curve of the second cycle were similar to the normal shape memory alloys, however, anomalies were observed in the heating curve of the first cycle. A significant increase of tensile strain started during heating at around 370 K (T_1 in Fig. 4(b)). It is also noted that the tensile strain started to decrease by further heating (i.e. the specimen shape recovered by further heating). This shape recovery by heating finished at around 500 K (T_2 in Fig. 4(b)) which is similar to the A_f of the second heating curve. These results suggest that the anomalies in the heating curve of the first cycle closely related to the martensitic transformation and its reversion upon heating.

In order to clarify the reason of the anomalies in the S-T curve of the (Ti-23Nb)-1.00 alloy during heating at the first cycle, in situ XRD measurements were carried out at 333 ~ 513 K under 200 MPa. Specimen temperature was kept constant during XRD measurements. The corresponding S-T curve during in situ XRD measurements and XRD profiles around the 112_β reflection peak of the parent β phase ($2\theta = 69.5 \sim 73.5$ deg.) were shown in Figs. 5 (a) and (b), respectively. It is noted that a remarkable increase of tensile strain appeared during the XRD measurement at D (393 K) as shown in Fig.5 (a). Figure 5 (b) shows that a distinct

reflection peak of $202_{\alpha''}$ appeared at 393 K and the intensity of 112_{β} reflection peak decreased by heating from C (373 K) to E (413 K). This implies that the formation of favorable martensite variants from parent β phase occurred by heating, and thus the increase in tensile strain during heating was due to the martensitic transformation. It is also noted that the shape recovery occurred by further heating, especially during heating from G (453 K) to I (493 K). The reflection peak of $202_{\alpha''}$ decreased by heating from G to I, whereas that of 112_{β} increased, implying that the shape recovery by heating from G to I is due to the reverse transformation from the α'' martensite phase to the parent β phase. Based on the above results, it is concluded that the sharp increase (C-E) and decrease (G-I) of tensile strain during heating are due to the martensitic transformation and its reverse transformation, respectively.

3.3. Heating-induced forward transformation

It is noteworthy that the heating-induced forward transformation (HIFT) from β phase to α'' martensite phase occurred in the (Ti-23Nb)-1.0O alloy as shown in Fig. 5. In general, forward martensitic transformation occurs during cooling instead of heating, however, the HIFT has been reported in several shape memory alloys such as NiMnIn [39], NiCoMnIn [40] and TiNi [41-43]. In case of the NiMn-base ferromagnetic shape memory alloys [39, 40], the forward martensitic transformation is kinetically arrested by a magnetic field. When the

specimen is cooled under a magnetic field, the forward martensitic transformation is suppressed and parent phase is maintained at low temperatures. This parent phase transforms to martensite phase by heating under zero magnetic field (i.e. HIFT). HIFT is also confirmed in the S-T curves of Ni-rich TiNi alloys. There have been debates about the origin of HIFT in the TiNi alloys, however, Ren et al. [42, 43] pointed out that the “strain glass” which was introduced by excess-Ni atoms plays a key role in the HIFT of TiNi alloys. On the other hand, HIFT in the (Ti-23Nb)-1.0O alloy originates from nanodomains which suppress the β - α martensitic transformation which occurs in the Ti-Nb alloys. As shown in Figs. 1 and 2, the nanodomain became unstable at high temperatures and almost disappeared above 373 K. This means that the suppression effect on the martensitic transformation by nanodomains disappeared above 373 K, and this temperature almost corresponds to the T_1 (HIFT start temperature) in Fig. 4(b). In the (Ti-23Nb)-1.0O alloy, therefore, the HIFT occurred and tensile strain increased above T_1 in the S-T curve.

An important feature of HIFT process in the Ti-Ni alloys is the presence of time dependence of the martensitic transformation. Niitsu et al. [41] pointed out that somewhat small defects or strain glass bring about the time dependence in the HIFT process of Ti-Ni alloys, however the detail mechanism of HIFT in Ti-Ni alloys is still unclear. Time dependence of the HIFT process in the (Ti-23Nb)-1.0O alloy was clearly confirmed by

following experiments. Figure 6 shows the S-T curves of the (Ti-23Nb)-1.0O alloy upon heating of the first cycle. Four specimens were heated under the same constant stress of 200 MPa with different heating rates of 2, 5, 10 and 20 K / min. T_1 and T_2 are plotted as a function of heating rate in the inset of Fig. 6. No significant difference was confirmed in T_2 and all of the heating curves during the reverse transformation overlapped. This means that the reverse transformation was not affected by the heating rate, i.e. there is no time dependence in the reverse transformation. On the other hand, T_1 decreased with decreasing heating rate. In addition, the amount of transformation strain during heating increased with decreasing heating rate. These results strongly indicate that the HIFT depends on time and it is a thermally-activated process. To clarify the mechanism of the thermally-activated process of HIFT in the (Ti-23Nb)-1.0O alloy, we estimated the activation energy of HIFT by using the Kissinger method, and it was determined to be 101 kJ / mol. This value is almost close to the reported activation energy between 107 and 158 kJ / mol for the oxygen diffusion in β phase of Nb-Ti-O alloys [44, 45]. Therefore, it is suggested that the thermally-activated process of HIFT in the (Ti-23Nb)-1.0O alloy involves oxygen diffusion.

The relationship between the HIFT and oxygen diffusion is explained as follows. As we reported in the previous paper [37], nanodomains generated by oxygen atoms suppress the progress of martensitic transformation at low temperatures, i.e. parent β phase was maintained

by nanodomains at lower temperatures. The relationship between the interstitial oxygen sites and induced nanodomain variants is shown in Fig. 7(a). Interstitial oxygen atoms at site 1, site 2 and site 3 introduce local strain fields along $[100]_\beta$, $[010]_\beta$ and $[001]_\beta$, respectively. These local strain fields introduced by oxygen atoms can be relaxed by the shuffling of $\{110\}_\beta$ planes to $\langle 1\bar{1}0 \rangle_\beta$ directions, and this shuffling forms each nanodomain [37]. There are six variants in the shuffling modes, i.e. nanodomains, and they depend on the direction of local strain fields which is determined by interstitial sites of oxygen atoms. When the tensile stress is not being applied to the specimen, the three types of interstitial sites distributed equivalently and randomly in the β phase: here the potential energy (E_i) and occupancy (O_i) between the three sites are equal ($E_1 = E_2 = E_3$ and $O_1 = O_2 = O_3$). Thus all of the six nanodomain variants form equivalently and they suppress the growth of other nanodomain variants, i.e. nanodomains act as local barriers to martensitic transformation. Figure 7(b) shows the oxygen atom at site 3 and the arrow along $[001]_\beta$ indicates the direction of the local strain field induced around the oxygen atom. In addition, the positions of nearest neighboring sites (site 1 and site 2) of the oxygen atom at site 3 are also indicated. Now the tensile stress is applied along $[1\bar{1}0]_\beta$ at a low temperature, the potential energy of each site changes ($E_1 = E_2 < E_3$), however, the occupancy rate of each site is still equal ($O_1 = O_2 = O_3$) because there is an energy barrier between each site which corresponds to the activation energy for oxygen diffusion. When the

specimen temperature increases and thermal energy becomes high enough to overcome the activation energy barrier, the occupancy rate for site 1 and site 2 becomes higher than that for site 3 ($O_1 = O_2 > O_3$). Change in the occupancy rate causes imbalance among nanodomain variants; $N_{V1} = N_{V2} = N_{V3} = N_{V4} < N_{V5} = N_{V6}$, where N_{Vi} is a number of nanodomain variant Vi . The imbalance among nanodomain variants weakens the effect of local barrier against the formation of long-ranged α'' martensite. In addition, the tensile stress along $[1\bar{1}0]_\beta$ enhances the growth of nanodomains of V6 because the lattice distortion strain of V6 is largest among six variants under the tensile stress along $[1\bar{1}0]_\beta$ (i.e. V6 is the most favorable variant when the tensile stress is applied along $[1\bar{1}0]_\beta$) [37]. As a result, it is supposed that the nanodomain variants of V1 ~ V5 switch to that of V6, then the long range martensitic transformation occurred by heating under tensile load along $[1\bar{1}0]_\beta$. This is the mechanism of HIFT we propose in the (Ti-23Nb)-1.0O alloy. The reverse transformation from α'' martensite to parent β phase occurs by further heating. The occupancy rates of site 1 and site 2 are still higher than that of site 3 ($O_1 = O_2 > O_3$) even after the reverse transformation because the tensile stress is being applied during the reverse transformation. During the cooling of the first cycle, therefore, nanodomains which suppress the martensitic transformation are not formed, then the favorable variant of α'' martensite is formed by cooling. This favorable variant of α'' martensite reverse-transforms to the parent β phase by heating again, with being accompanied

by the decreased of strain. Therefore, there is no anomaly in the cooling curve of the first cycle and heating curve of the second cycle.

To clarify the effect of applied stress on HIFT of (Ti-23Nb)-1.0O alloy, the S-T mode tensile tests were carried out under various stresses from 150 MPa to 300 MPa, and the results are shown in Fig. 8(a). Different specimens were used for each tensile test and heating / cooling rate was ± 10 K / min. The amount of transformation strain by HIFT increased with increasing tensile stress. When the applied constant stress was 150, 200 and 250 MPa, the transformation strain by HIFT was completely recovered by the reverse transformation; however, the shape recovery by reverse transformation became incomplete at the constant stress of 300 MPa. This is due to the introduction of plastic deformation during HIFT and following reverse transformation upon heating. The relationships between the applied stress and T_1 and T_2 are shown in Fig. 8(b). The A_f of Ti-23Nb alloy at 0MPa determined by DSC is also plotted in Fig. 8(b) for comparison. With increasing applied constant stress, T_1 slightly decreased, this can be explained by the stress-assisted diffusion of oxygen atoms. On the other hand, T_2 increased with increasing applied constant stress, which is consistent with the Clausius-Clapeyron relationship. The slope of the linear relationship was determined to be 3.3 MPa / K, and this is almost similar to the other Ti-Nb base shape memory alloys [3, 10, 19, 21]. In addition, A_f of the Ti-23Nb alloy at 0 MPa lay on the extrapolated line of T_2 . These results

also support that the increase of strain upon heating is associated with the thermally activated process assisted by applied stress, whereas the recovery of tensile strain is due to the reverse transformation.

3.4. Shape memory effect and superelasticity

Figure 9 shows the S-S curves of (a) the Ti-23Nb and (b) (Ti-23Nb)-1.0O alloys obtained at the temperature range of 173 ~ 573 K. Specimen temperature was kept constant for 0.3 ks before each tensile test in order to achieve an equilibrium condition and strain rate was $2.5 \times 10^{-4} \text{ s}^{-1}$. After unloading, all of specimens were heated up to 673 K, and dashed lines with an arrow in Fig. 9 indicate the shape recovery by heating. At the temperature range between 173 K and 373 K, the Ti-23Nb alloy exhibited the shape memory effect (SME). On the other hand, both of SME and superelasticity (SE) were partially observed in addition to partial plastic deformation (PD) at 423 K. With further increasing test temperature above 423 K, the Ti-23Nb alloy exhibited only PD. SE was expected at 473 K in the Ti-23Nb alloy because the A_f of Ti-23Nb alloy was 422 K [37], however, only PD was observed. It is also noted that the S-S curve at 473 K reveals the higher yield stress compared with other test temperatures. This is due to the formation of isothermal- ω phase which precipitated during heating the specimen and holding the test temperature before the tensile test. The precipitation

of isothermal- ω phase in Ti-base alloys decreases the martensitic transformation temperatures due to the enrichment of solute atoms in the β matrix [1, 46], thus only the PD was confirmed at 473 K. Except the precipitation of isothermal- ω phase, the temperature dependence of shape memory behavior in the Ti-23Nb alloy is consistent with the other shape memory alloys such as Ti-Ni and Cu-base alloys [47].

On the other hand, curious temperature dependence of shape memory behavior was observed in the (Ti-23Nb)-1.0O alloy. With increasing test temperature from 173 K to 573 K, the shape memory behavior changed as follows; SE (173 ~ 323 K), SME (323 ~ 423 K), SE (473 K) and PD (523 ~ 573 K). The apparent yield stress (σ_y) of each S-S curve of the (Ti-23Nb)-1.0O alloy is plotted as a function of test temperature in Fig. 10, and T_1 and T_2 determined by S-T curves are also shown in Fig. 10 for comparison. SE at low temperature (173 ~ 323 K) is due to the growth of favorable nanodomain variants and continuous increase in the lattice distortion of the favorable nanodomain variants [37]. Martensitic transformation was suppressed by nanodomains at lower temperatures, thus the mechanism of SE at 173 ~ 323 K was different with the other normal shape memory alloys such as oxygen-free Ti-Nb and Ti-Ni alloys. It is noted that SME was observed between 323 K and 423 K and this temperature range is almost similar to the temperatures at which the HIFT was confirmed in S-T curves. In addition, the recovery of remained strain after unloading finished at 453 K (Fig. 11),

this temperature is almost consistent with $A_f(T_2)$ at 0 MPa. Thus it is suggested that the origin of the SME at 323 ~ 423 K is similar to that of HIFT in S-T curve, i.e. an imbalance of interstitial oxygen sites ($O_1 = O_2 > O_3$) occurred during tensile deformation and suppression effect against martensitic transformation by nanodomains became weaker, then a favorable variant of long-ranged α'' martensite (V6) formed. This favorable variant of α'' martensite remained after unloading because the reverse transformation temperature is higher than 423K, and reverse transformed to the parent β phase by heating above $A_f(T_2)$, thus the SME was confirmed at 323 ~ 423 K. While the long-ranged α'' martensite was also formed by tensile deformation at 473 K, the reverse transformation by unloading (SE) occurred because the test temperature (473 K) was higher than the $A_f(T_2)$ at 0 MPa. The mechanism of this SE at 473 K is similar to that of the normal shape memory alloys. Above 523 K the deformation occurred by slip (PD), thus the neither the SME nor SE was confirmed.

As mentioned in the previous sections, T_l determined by S-T curves depends on heating rate, i.e. the formation of long-ranged α'' martensite by diffusion of oxygen atoms depended on time. This time dependence of HIFT in S-T curves corresponds to the strain rate dependence of shape memory behaviors in S-S curves. Tensile tests were carried out for the (Ti-23Nb)-1.0O alloy at 353 K with strain rate of 2.5×10^{-3} , 2.5×10^{-4} and $2.5 \times 10^{-5} \text{ s}^{-1}$, respectively. All the specimens were heated up to about 500 K after unloading. Figure 12

shows the obtained S-S curves and dashed lines with an arrow indicate the shape recovery by heating. Strain rate dependence of shape memory behavior was clearly confirmed: SE was observed at higher strain rates while SME was observed at lower strain rates. These strain rate dependence of shape memory behavior can be explained by the oxygen diffusion which is the origin of time dependence in the HIFT process of the (Ti-23Nb)-1.0O alloy. At 353 K, nanodomains (the lattice modulation) became unstable but still existed before loading as shown in Figs. 1 and 2. When the strain rate was fast and tensile deformation finished in a short time, the diffusion of oxygen atoms in nanodomains is difficult to occur during the tensile test, thus the occupancy rates at three interstitial oxygen sites were equal during the tensile deformation ($O_1 = O_2 = O_3$). As a result, therefore, unfavorable variants of nanodomains (= local barriers against the long ranged martensitic transformation) remained during the tensile deformation, and they suppressed the rapid growth of favorable variants of nanodomains. Thus the inelastic strain by the continuous growth of favorable variants of nanodomains occurred during the tensile deformation. Occupancy rates at three oxygen sites were also equal ($O_1 = O_2 = O_3$) during unloading, therefore, all of the six variants of nanodomains returned back to the initial state (= six variants of nanodomains distributed equivalently and randomly in the specimen) by unloading, this corresponds to the shape recovery by unloading. This is the mechanism of SE obtained at the highest strain rate in the S-S mode tensile tests. On the other hand, in case of

the lowest strain rate, there was enough time for the oxygen diffusion, thus the occupancy rates at oxygen sites changed during the tensile deformation and long-ranged α'' martensite (favorable variant) was formed. This α'' martensite remained after unloading and reverse transformed to the parent β phase by heating above T_2 (A_f), then the residual strain recovered (SME). With decreasing strain rate the apparent yielding stress decreased, this implies that the formation of α'' martensite easily occurred at a lower tensile stress compared with the growth of favorable nanodomain variants. In other words, higher tensile stress is required for the growth of favorable nanodomain variants to overcome the local barriers induced by the unfavorable nanodomain variants.

Figure 13 shows the schematic diagram showing the phase transformation and shape memory behavior of the (Ti-23Nb)-1.0O alloy. High temperature β phase is maintained at lower temperatures by the six variants of nanodomains which distributed randomly and homogeneously in β phase. With increasing temperature, nanodomains in β phase become faint, and β phase (without nanodomains) is obtained. Diffusion of oxygen atoms in nanodomains occurs in the transient region, thus the phase transformation and shape memory behavior in this region depend on time. The mechanism of SE at higher temperatures ($T_2 < T < T_s$) is different from that of lower temperatures, i.e. it is due to the stress-induced martensitic transformation by loading and its reversion by unloading. Temperature dependence of σ_y is

also shown in Fig. 13, and they can be divided into five regions (I) ~ (V). In regions (I) and (II), the deformation occurs by gradual growth of favorable nanodomain variants. With increasing temperature the σ_y decreased in region (I) and increased in region (II). The decrease of σ_y by heating in region (I) is due to the weakness of local barriers by nanodomains at higher temperatures (i.e. favorable variants of nanodomains easily grow when the local barrier is small). In region (II), the σ_y increased with increasing temperature, this implies that the higher tensile stress was necessary for the growth of favorable nanodomain variants at higher temperatures, which is consistent with the Clausius-Clapeyron relationship. Deformation mechanism and σ_y in region (III) depend not only on temperature but also on time. When the oxygen diffusion occurs enough during the tensile test (i.e. the tensile deformation is carried out at higher temperatures and/or low strain rates), long-ranged α'' martensite is formed by tensile stress and σ_y decreases. In region (IV), the stress-induced martensitic transformation occurs from β phase to α'' phase, thus the temperature dependence of σ_y follows the Clausius-Clapeyron relationship. The σ_y decreases with increasing test temperature above T_s because the tensile deformation occurs by slip in region (V). Consequently, it is concluded that diffusion of oxygen atoms and stability of nanodomain variants bring about the unique martensitic transformation and shape memory behavior such as the HIFT and time dependent shape memory behavior.

4. Conclusions

Temperature dependence of lattice modulation (nanodomains) which was introduced by oxygen atoms and martensitic transformation behavior of the (Ti-23Nb)-1.0O alloy were systematically investigated by TEM observation, in situ XRD measurements and tensile tests. Effects of nanodomains and oxygen atoms on shape memory behavior were discussed. The obtained results were summarized as follows.

1. Local lattice modulation (nanodomains) in the β phase was stable at low temperature (90 K) whereas unstable at higher temperatures and disappeared above 373 K. Observed lattice modulation mode is equal to the shuffling process involved in the β - α'' martensitic transformation, therefore, the stability of the lattice modulation in the (Ti-23Nb)-1.0O alloy is similar to that of α'' martensite in the Ti-23Nb alloy.
2. Time-dependent heating-induced forward transformation (HIFT) was confirmed by the strain-temperature (S-T) mode tensile tests of the (Ti-23Nb)-1.0O alloy. Activation energy for HIFT was determined to be 101 kJ / mol which is almost equal to that for the diffusion of oxygen atoms in β -Ti alloys. Thus the time-dependent HIFT originates from the diffusion of oxygen atoms in nanodomains and the resulting imbalance of nanodomain variants during heating under tensile stress. Local barriers against the long-ranged α''

martensite by random variants of nanodomains were destroyed by the imbalance of nanodomain variants then long-ranged α'' martensite was formed by heating (i.e. HIFT), and the thermally-activated process of HIFT involves the diffusion of oxygen atoms in nanodomains.

3. Due to the diffusion of oxygen atoms and following HIFT, anomalous temperature dependence of shape memory behavior was confirmed by the stress-strain (S-S) mode tensile tests in the (Ti-23Nb)-1.0O alloy. Time-dependent shape memory behavior was also confirmed in the stress-strain curves obtained at 353 K, this is due to the diffusion of oxygen atoms during the tensile deformation.

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Fig. 1 Selected area diffraction patterns (SADPs) of the (Ti-23Nb)-1.0O alloy obtained at (a) 90 K, (b) 293 K, (c) 353 K, (d) 373 K and (e) 423 K. All SADPs were taken from the same region in the same grain and zone axis was $[001]_{\beta}$.

Fig. 2 Intensity profiles of diffraction spots along (a) $[110]_{\beta}^*$ and (b) $[1\bar{1}0]_{\beta}^*$.

Fig. 3 DSC curves for the Ti-23Nb and (Ti-23Nb)-1.0O alloys [37].

Fig. 4 (a) Procedure of strain-temperature mode tensile test. (b) Strain-temperature curves of the (Ti-23Nb)-1.0O alloy. Inset shows the typical strain-temperature curves of normal shape memory alloys.

Fig. 5 In situ XRD measurements for the (Ti-23Nb)-1.0O alloy at the temperature range of 333 ~ 513 K under 200 MPa. (a) Corresponding strain-temperature curve and (b) obtained XRD profiles.

Fig. 6 Heating rate dependence of strain-temperature curves of the (Ti-23Nb)-1.0O alloy.

Inset shows the changes of T_1 and T_2 .

Fig. 7 (a) Relationship between the interstitial sites (site 1-3) and nanodomain variants (V1-V6). (b) Schematic illustration explaining the effect of tensile load along $[1\bar{1}0]_\beta$ on the interstitial oxygen positions.

Fig. 8 Effect of applied stress on (a) the strain-temperature curves and (b) T_1 and T_2 of the (Ti-23Nb)-1.0O alloy. The A_f of Ti-23Nb alloy at 0 MPa determined by DSC (Fig. 3) was also plotted for comparison.

Fig. 9 Stress-strain curves obtained at various temperature for the (a) Ti-23Nb and (b) (Ti-23Nb)-1.0O alloys.

Fig. 10 Test temperature dependence of apparent yield stress (σ_y) for the (Ti-23Nb)-1.0O alloy.

Fig. 11 Shape recovery by heating for the (Ti-23Nb)-1.0O alloy tensile tested (stress-strain mode) at 373 K (Fig. 9(b)).

Fig. 12 Effect of strain rate on the stress-strain curves of the (Ti-23Nb)-1.0O alloy.

Fig. 13 Schematic diagram explaining the phase transitions and shape memory behavior of the (Ti-23Nb)-1.0O alloy.

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