Significantly fast spinodal decomposition and inhomogeneous nanoscale martensitic transformation in Ti–Nb–O alloys

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The β phase spinodal decomposition during continuous cooling in Ti–Nb–O alloys is investigated by the phase-field method. Addition of only a few at.% O to Ti–23Nb (at.%) alloy remarkably increases the driving force of the β phase spinodal decomposition. During isothermal heat treatment at 1000 K and 1100 K in Ti–23Nb–30 (at.%) alloy, the β phase separates into β0 phase denoted as (TiO)(O, Nb) and β2 phase denoted as (Ti, Nb)3(O, Nb)2, resulting in the formation of nanoscale concentration modulation. The phase decomposition progresses in 0.3–20 ms. In Ti–23Nb–XO alloys (X = 1.0, 1.2, 2.0), the spinodal decomposition occurs during continuous cooling with the rate of 500 K s⁻¹, indicating that the spinodal decomposition occurs during water quenching in the alloys. It is assumed that there is a threshold value of oxygen composition for inducing the spinodal decomposition because it does not occur during continuous cooling in Ti–23Nb–0.6O (at.%) alloy. The concentration modulation introduced by the β phase decomposition has significant effect on the β→α² martensitic transformation. Hence, it seems that for controlling microstructure and mechanical properties of Ti–Nb–O alloys, careful control of heat treatment temperature and cooling rate condition is required.

1. Introduction

Some β-type Ti–Nb alloys have shape-memory and superelasticity properties and are applied to biomedical materials [1-3]. The shape-memory and superelasticity properties of the alloys are derived from the martensitic transformation (MT) from the β phase (with a body-centered cubic lattice) to the α² phase (with a face-centered orthorhombic lattice). Miyazaki et al. have reported that in oxygen added Ti–Nb alloys, the long-range MT is suppressed and the nanoscale lattice-modulated domain is formed instead, which is called nanodomains [4-8]. In general, the oxygen is known as a typical α-stabilizing element and its addition to Ti-based alloys is assumed to promote the MT from the β phase to the α² phase (or α phase with a hexagonal lattice). Hence, effects of the oxygen addition on the MT and the nanodomain formation have long been unclear [6,7,9].

In a previous phase-field simulation study, we proposed that the nanodomain formation can be explained by the diffusional-displacive transformation [10]. The oxygen addition to a Ti–Nb alloy promotes the nanoscale spinodal decomposition of the β phase into Nb-lean β0 phase and Nb-rich β2 phase at 1073 K or 1173 K, which are typical homogenization temperatures of Ti–Nb-based alloys. Because of the difference of Nb concentration between the β0 and β2 phases, the selective β0→α² MT occurs at 300 K, resulting in the nanodomain formation.

The phase separation occurs in Ti–Ta [11], Ti–Mo [12] and Ti–Nb alloys [13]. In Ti–Nb binary system, the β phase separation region does not exist in the equilibrium phase diagram but it appears in the metastable phase diagram considering only the β and α² phases [14]. The spinodal decomposition in Ti–Nb-based alloys has been observed experimentally in a Ti–Nb–Ta–Zr alloy via three-dimensional atom-probe tomography [15,16]. It has been suggested that the MT behavior and mechanical properties of the Ti–Nb–O alloy remarkably increases the driving force of the β phase spinodal decomposition. During isothermal heat treatment at 1000 K and 1100 K in Ti–23Nb–30 (at.%) alloy, the β phase separates into β0 phase denoted as (TiO)(O, Nb) and β2 phase denoted as (Ti, Nb)3(O, Nb)2, resulting in the formation of nanoscale concentration modulation.

2. Calculation method

The field variable $z_X(r,t)$ is defined using the mole fraction $x_X(r,t)$ as follows [19]:

$$
\frac{\partial z_X(r,t)}{\partial t} = \frac{x_X(r,t)}{1 - x_O(r,t)}, \quad (X = Ti, Nb, O) \quad (1)
$$

where $X$ denotes the components ($X = Ti, Nb, O$), and $r$ and $t$ denote positional vector and time, respectively. The $z_{AS}(r,t)$ and $z_{BS}(r,t)$ are regarded as independent variables, and their temporal evolution is calculated by the Cahn–Hilliard equation as follows [20]:

$$
\frac{\partial z_X(r,t)}{\partial t} = \nabla \cdot \left[ M_X \nabla \left( \frac{\delta G_{sys}}{\delta z_X(r,t)} \right) \right] \quad (2)
$$

where $G_{sys}$ is the total free energy of the system, and $M_X$ is the diffusion mobility of the component $X$. The $G_{sys}$ is defined by

$$
G_{sys} = \int \left\{ \frac{G_{\beta}^X}{X = Ti, Nb, O} + \sum_{X = Ti, Nb, O} \frac{\kappa_X}{2} \left( \nabla z_X \right)^2 \right\} dr \quad (3)
$$

where $G_{\beta}^X$ is the Gibbs energy of the β phase and $\kappa_X$ is the gradient energy coefficient. For simplicity, the values of $\kappa_X$ for all components are assumed to be identical. Based on the CALPHAD method, the $G_{\beta}^X$ is formulated using the two-sublattice model [18], (Nb, Ti)3(O, Nb)2, where $V_0$ denotes the vacancy. The thermodynamic parameters of the phase diagram of the Ti–Nb–O system are used [21-24]. The $M_X$ is related to the impurity diffusion coefficient, $D_{imp}$ or $D_{Nb}$ [19,25].

In this study, one-dimensional simulation was performed for the length scale of 20 nm by using 64 computational grids, and the periodic boundary condition was assumed. The Cahn–Hilliard equation (Eq. (2)) was solved by the conventional finite difference method with explicit Euler technique. In the simulation under the water quenching condition, the temperature was decreased from 1200 K to 300 K with the cooling rate of 500 K s⁻¹. The simulation condition is schematically shown in Fig. 1.
3. Results and discussion

The β phase separations in Ti–23Nb–3O (at.%) alloy during isothermal heat treatments are calculated and the results are shown in Fig. 2. Fig. 2a and 2b show the simulation results at 1100 K and 1000 K, respectively. At both temperatures, the β phase separates into Nb-lean β₁ phase and Nb-rich β₂ phase. The composition of the β₁ phase is Nb-lean, Ti-rich and O-rich, while that of the β₂ phase is Nb-rich and O-lean. Using the sublattice model, the β₁ and β₂ phases can be expressed as (Ti)₁(O, Va)₃ and (Nb, Ti)₁(Va)₃, respectively. The concentration modulation is introduced by the spinodal decomposition in 0.3 ms at 1100 K and in 1.0 ms at 1000 K. The compositional difference between the β₁ and β₂ phases and the wave length of the concentration modulation increase with time. It is seen that the compositional difference between the β₁ and β₂ phases at 1000 K is slightly larger than that at 1100 K, and the spinodal decomposition at 1000 K takes more time than that at 1100 K. The calculation results show that in Ti–23Nb–3O (at.%) alloy, the β phase spinodal decomposition progresses in 0.3–20 ms at 1000–1100 K during the cooling process. When the alloy is water quenched with the cooling rate of 500 K s⁻¹, the decrement of 100 K takes 0.2 s, implying that the spinodal decomposition can occur at 1000–1100 K. The atomic diffusion during water quenching is often ignored but in Ti–Nb–O alloys, it is presumed that the β phase spinodal decomposition occurs even during water quenching.

In order to investigate the spinodal decomposition behavior during water quenching, the phase-field simulation was performed under the continuous cooling condition with the cooling rate of 500 K s⁻¹. Figure 3 shows the change in the concentration profile during the continuous cooling in Ti–23Nb–1O alloy. The concentrations of all components are homogeneous at 1200 K and 1100 K, and the concentration modulation is observed at temperatures below 1000 K. The β phase spinodal decomposition progresses at 1100–800 K, and the concentration profile at 800–300 K undergoes very little change.

Figure 4 shows the partial longitudinal section of the metastable phase diagram considering only the β phase in Ti–Nb–O system. In the figure, the Nb composition is fixed to 23at.% and the spinodal line is shown by the dashed line. The temperature of the binodal line increases from about 700 K (Ti–23Nb) to 1150 K (Ti–23Nb–1O) and to
above 1400 K (Ti–23Nb–20) with increasing O composition, indicating that the addition of a few at.% O to Ti–23Nb alloy induces the β phase decomposition. We see from Fig. 4 that the three-phase region exists at 670–790 K. The calculation results of compositions and fractions of the three β phases in Ti–23Nb–1O alloy are shown in Fig. 5a and 5b, respectively. In this study, Nb-rich phase that appears at temperatures below 750 K is called as β2' phase. With decreasing temperature, the β2' phase appears at about 750 K and the β2 phase disappears at 670 K. Compared to the β1 phase, both β2 and β2' phases are Nb-rich; however, the compositions of the β2 and β2' phases are clearly different from each other. The β2 phase is Ti–Nb-based phase with little oxygen. On the other hand, the β2' phase is Nb-based phase with little oxygen. Using the sublattice model, the β1, β2 and β2' phases can be expressed as $(Ti)(O,V_{a})_{3}$, $(Nb, Ti)(V_{a})_{3}$ and $(Nb)(V_{a})_{3}$, respectively. The O composition of the β1 phase in the β1 + β2' region is lower than that in the β1 + β2 region (see Fig. 5a), and the fraction of the β1 phase in the β1 + β2' region is higher than that in the β1 + β2 region (see Fig. 5b). Hence, microstructures that are formed during isothermal heat treatments in the β1 + β2 and β1 + β2' regions would be quite different from each other.

Figure 6 shows the change in the concentration distribution during continuous cooling with the rate of 500 K s⁻¹ in Ti–23Nb–1O alloy; the concentration data is extracted from the simulation results shown in Fig. 3. In Fig. 6, the tie line is shown by solid line at each temperature. At 700 K, the alloy composition is inside the three-phase region and hence the three-phase triangle is shown instead of the tie line. In Ti–23Nb–1O alloy, the temperature of the spinodal line is 1090 K. However, we see from Fig. 6 that the spinodal decomposition does not occur at 1050 K during the continuous cooling. The spinodal decomposition progresses at 1050–800 K along the tie lines. As shown in Fig. 5, in Ti–23Nb–1O alloy, there is the β1 + β2 phase at temperatures above 750 K, while the β1 + β2' appears at temperatures below 670 K; this is also seen in Fig. 6 because the tie lines at 1050–800 K and 600–400 K are clearly different from each other. The concentration distribution slightly changes at 700–400 K and does not coincide with the tie line of the β1 + β2' phase. This result indicates that during the continuous cooling, the concentration modulation introduced by the spinodal decomposition at high temperatures is maintained at low temperatures.

The effect of O composition of the alloy on the spinodal decomposition behavior during the continuous cooling was investigated by phase-field simulations. Figure 7 shows the change in the concentration profile during continuous cooling with the rate of 500 K s⁻¹ in Ti–23Nb–XO alloys (X = 0.6, 1.2, 2.0). The phase decomposition does not occur in Ti–23Nb–0.6O alloy, indicating that there is a critical value of O composition for inducing the spinodal decomposition during water quenching. The concentration
modulation is observed in Ti–23Nb–1.2O alloy at 1100 K, while the spinodal decomposition occurs at 1200 K in Ti–23Nb–2.0O alloy. The spinodal decomposition temperature increases as the O composition increases.

In order to understand the relationship between the β phase spinodal decomposition and the β→α” MT, the driving force of the MT, ΔG_MT, corresponding to the concentration profiles at 300 K shown in Figs. 3 and 7 was investigated. The ΔG_MT is defined as ΔG_MT = G_c^β - G_c^α; the α” phase is more stable than the β phase when ΔG_MT > 0, while the β phase is more stable than the α” phase when ΔG_MT < 0. In our calculation, because of the lack of experimental data, the Gibbs energy of the α phase (G_c^α) is used instead of G_c^α”. The concentration profiles of Ti–23Nb–XO alloys (X = 1.0, 1.2, 2.0) and the corresponding ΔG_MT profiles are shown in Fig. 8a and 8b, respectively. In Ti–23Nb–1.0O and Ti–23Nb–1.2O alloys, ΔG_MT > 0 in the entire region. However, the β phase stability in the Nb-rich region (β2 phase) is extremely higher than that in the Nb-lean region (β1 phase). This is due to the fact that Nb is one of the typical β-stabilizing elements. In Ti–23Nb–2.0O alloy, nanoscale distribution of the α” phase stable region (ΔG_MT > 0) and the β phase stable region (ΔG_MT < 0) can be seen. Note that ΔG_MT is not so influenced by the average composition of the alloy (see dash-dot line in Fig. 8b) but rather is influenced by the degree of the concentration modulation introduced during water quenching. Therefore, careful design of heat treatment and cooling rate conditions is assumed to be necessary to control the β→α” MT behavior and the mechanical properties of Ti–Nb–O alloys.

4. Conclusions

The β phase spinodal decomposition during continuous cooling in Ti–Nb–O alloys was investigated by the phase-field method. The obtained results are as follows.

1. Oxygen addition to the alloy promotes the β phase spinodal decomposition to Nb-rich and Nb-lean phases. In Ti–23Nb–3O (at.%), the β phase separates into the nanoscale β1 and β2 phases that can be expressed as (Ti)1(O, Va)3 and (Nb, Ti)1(Va)3, respectively, during isothermal heat treatment at 1100 K and 1000 K. The spinodal decomposition progresses in 0.3–20 ms at 1000–1100 K.

2. In Ti–23Nb–XO alloys (X = 0.1–3.0), the three-phase region of the β1, β2 and β2’ phases exists at 670–790 K. The β2’ phase can be expressed as (Nb)1(Va)3. In Ti–23Nb–1O alloy, the tie line of the β1 + β2 phase at temperatures above 750 K is clearly different from that of the β1 + β2’ phase at temperatures below 670 K.

3. The β phase spinodal decomposition in oxygen-added Ti–23Nb (at.%) alloys occurs during continuous cooling with the rate of 500 K s⁻¹, indicating that the spinodal decomposition progresses during water quenching. The concentration modulation introduced by the β1 + β2 spinodal decomposition at 1050–800 K is maintained at lower temperatures during the continuous cooling. The β phase spinodal decomposition has significant effect on the β→α” MT. Hence, careful design of heat treatment and cooling rate conditions is assumed to be necessary to control the mechanical properties of Ti–Nb–O alloys.

5. Acknowledgement
This work was partly supported by the research grant from Kyosho Hatta Foundation.

6. References

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