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Phase-field simulation of spinodal decomposition and its effect on stress-induced martensitic transformation in Ti–Nb–O alloys

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A B S T R A C T

In this study, the phase-field method was used to simulate the spinodal decomposition of the β phase in Ti–23Nb–*X*O (atomic percent (at.%)) alloys (X = 1, 2, 3, 4, and 5) at 1073 K and the subsequent stress-induced β → α” martensitic transformation (MT) at 300 K. At 1073 K, the β phase separates into an O-rich β_1 phase and an O-lean β_2 phase in some Ti–23Nb–*X*O alloys (X = 2, 3, 4, and 5). The tendency toward phase decomposition increases with an increase in oxygen content. When an external tensile stress of 240–270 MPa is applied to certain Ti–23Nb–*X*O alloys (X = 1, 2, and 3) along the $[0\,1\,1]_\beta$ direction at 300 K, a stress-induced β → α” MT occurs. In Ti–23Nb–*X*O alloys (X = 4 and 5), the β_1 → α” MT first occurs at 50–110 MPa and the nanoscale α” phase with a size of around 2 nm is formed, reflecting the (β_1 + β_2) microstructure. This change is followed by a β_2 → α” MT at 660 MPa in Ti–23Nb–4O alloy; however, the β_2 → α” MT does not occur even with an external tensile stress of 800 MPa applied along the $[0\,1\,1]_\beta$ direction in Ti–23Nb–5O alloy. Further, the calculated hysteresis loop of the stress–strain (S–S) curve at 300 K becomes slim as the oxygen content increases. It is therefore concluded that the S–S characteristics of Ti–Nb–O alloys are strongly influenced by the (β_1 + β_2) microstructure, which gives rise to a nanoscale heterogeneity of the driving force for the β → α” MT.

1. Introduction

β-type Ti–Nb alloys exhibit superior shape-memory properties, superelasticity, and corrosion resistance and have, therefore, been applied as biomedical materials [1,2]. The shape memory and superelasticity are derived from a martensitic transformation (MT) from the β phase (with a body-centered cubic (bcc) lattice) to an α” phase (with a face-centered orthorhombic (fco) lattice). The effects on the mechanical properties and microstructure of the materials after adding oxygen to Ti–Nb alloys have been systematically investigated [3–7]. As the oxygen content increases, the hysteresis loop of the stress–strain (S–S) curve changes its shape from sharp and wide to round and slim [4]. The microstructure of oxygen-added Ti–Nb-based alloys was investigated using transmission electron microscopy (TEM); the interstitial oxygen atoms induce the formation of nanometer-sized martensite (with nanodomains or nanoscale modulated domains), which is homogeneously and randomly distributed in the β phase [4–7]. As the oxygen content increased, the nanodomains increased in both size and number and eventually spread throughout the Ti–26Nb–1.0O (at.%) alloy specimen [4].

The modulated structure observed in Ti–23Nb–1O (at.%) alloy has a $\{110\}_\beta\langle 1\bar{1}0\rangle_\beta$ displacement [5] that corresponds to the shuffling mode of the β → α” MT. The relaxation of the local strain induced by the interstitial oxygen atoms is related to the shuffling modes. The six shuffling modes (six variants of nanodomain) can exist in equal proportions when an external stress is not applied [5]. The application of external stress promoted the growth of a specific nanodomain variant, thereby reducing the strain energy. The existence of six nanodomain variants and their preferential growth [5,8,9] according to the stress state may explain not only the deformation mechanism of superelastic oxygen-added Ti–Nb-based alloys but also that of gum metal, which exhibits a low elastic modulus, high strength, and large elastic strain [10].

Based on the first-principles density functional theory, the interaction between the interstitial oxygen atoms in β-Ti_3Nb and the lattice distortion and β → α” transformation caused by the oxygen atoms was investigated [11]. Owing to the $\{110\}_\beta\langle 1\bar{1}0\rangle_\beta$ shuffling, Ti_6Nb_2O is metastable and comprises a lattice approximately halfway between β and α” structure. The theoretical calculations suggest that the oxygen was not uniformly distributed in oxygen-added Ti–Nb based alloys but were instead concentrated in nanodomains with a typical content of approximately 11 at.%. However, the reason for the homogeneous and random distribution of nanoscale high-oxygen regions in the β phase remains unclear. As will be demonstrated in this study, oxygen addition to the Ti–Nb-based alloys induces spinodal decomposition of the β

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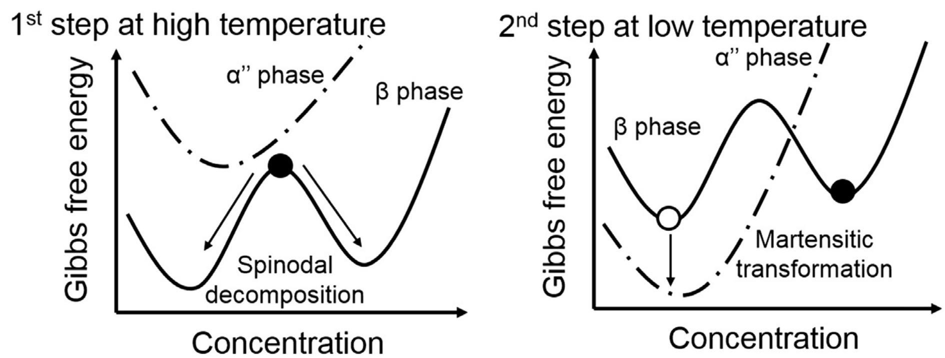

Fig. 1. Gibbs free energy curves showing a possible scenario of the formation of nanodomains in Ti–Nb–O alloys: spinodal decomposition at a high temperature (left) and the subsequent martensitic transformation at a low temperature (right).

phase; when the specimen is heat treated at 1073 or 1173 K [4,5], the β phase can separate into nanoscale O-rich β_1 and O-lean β_2 phases. If the β_1 phase selectively transforms to the α" phase (or the Ti_6Nb_2O semi-α" phase [11]), it is presumed that nanodomains are homogeneously and randomly formed in the β phase, reflecting the nanoscale (β_1 + β_2) spinodal microstructure. Fig. 1 shows schematic of the hypothesized spinodal decomposition of the β phase and the subsequent $\beta_1 \rightarrow$ α" MT.

The phase-field method is a powerful computational approach for modeling microstructure evolution in materials with the use of thermodynamic parameters of Gibbs free energy behind the phase diagram [12,13]. When the contribution of elastic strain energy is considered in a phase-field model, effect of the long-range elastic interaction on the microstructure evolution can be predicted [12]. In this study, microstructure evolution associated with the spinodal decomposition of the β phase in Ti–23Nb–*X*O (at.%) (X = 1, 2, 3, 4, and 5) alloys at 1073 K and the subsequent β → α" MT under external stress at 300 K is investigated using the conventional phase-field method [12]. We aim to acquire the fundamental knowledge about the S–S response when one of the six nanodomain variants is formed; this is the first step for fully understanding the effects of the existence of six nanodomain variants on mechanical properties in the future. The Gibbs free energy of each phase is formulated based on conventional sublattice model [14] using the thermodynamic parameters of the Ti–Nb–O system. The β → α" MT behavior cannot be explained solely by the Gibbs free energy behind the equilibrium phase diagram (shown in Fig. 1) because the elastic strain energy of microstructure influences the transformation behavior. Hence, the elastic strain energy is calculated based on the microelasticity theory [15,16] and the elastic field arising from the β → α" transformation strain is explicitly considered. The influence of oxygen content on the spinodal decomposition of the β phase at 1073 K is characterized. An external stress is then applied to the (β_1 + β_2) microstructure, and the β → α" MT at 300 K is calculated. The macroscopic strain along the external stress axis is calculated to obtain overall S–S curve, and the effect of (β_1 + β_2) microstructure on the shape of the S–S curve is explored.

2. Calculation method

2.1. Gibbs free energy

The Gibbs free energies of the β and α" phases are described based on two-sublattice model for interstitial solid solutions [14]. Because of the lack of experimental data, the Gibbs free energy of the α" phase is assumed to be identical to that of the α phase, whereas the actual Gibbs free energy of the α" phase is presumed to be higher than that of the α phase. When the interstitial sites are occupied by oxygen atoms or vacancies (Va) in the Ti–Nb–O system, the sublattice model of phase A (A = α" or β) is represented by $(\mathrm{Nb,Ti})_{p^A}(\mathrm{O,Va})_{q^A}$, where p^A and q^A are the site numbers of the first sublattice (corresponding to the substitutional sites) and the second sublattice (corresponding to the interstitial sites), respectively. Here $p^A = 1$ and hence q^A is the number of interstitial site per one substitutional site. Assuming that oxygen occupies the octahedral interstitial sites, we describe the sublattices of β and α phases as $(\mathrm{Nb,Ti})(\mathrm{O,Va})_3$ and $(\mathrm{Nb,Ti})(\mathrm{O,Va})_{0.5}$, respectively. The Gibbs free energy of phase A, G_c^A, is given by

$$G_c^A = \sum_{X_\mathrm{I}=\mathrm{Nb,Ti}} \sum_{X_\mathrm{II}=\mathrm{O,Va}} y_{X_\mathrm{I}}^{\mathrm{I}} y_{X_\mathrm{II}}^{\mathrm{II}}\, {}^{\circ}G_{X_\mathrm{I}:X_\mathrm{II}}^{A} + {}^{\mathrm{ex}}G + \mathrm{R}T\left[p^A \sum_{X_\mathrm{I}=\mathrm{Nb,Ti}} y_{X_\mathrm{I}}^{\mathrm{I}} \ln y_{X_\mathrm{I}}^{\mathrm{I}} + q^A \sum_{X_\mathrm{II}=\mathrm{O,Va}} y_{X_\mathrm{II}}^{\mathrm{II}} \ln y_{X_\mathrm{II}}^{\mathrm{II}}\right], \tag{1}$$

where $y_{X_m}^m$ is the site fraction of component X_m in sublattice m; ${}^{\circ}G_{X_\mathrm{I}:X_\mathrm{II}}^{A}$ is the Gibbs free energy when the first and second sublattices are occupied by the X_I and X_II components, respectively; R is the gas constant; T is the absolute temperature; and ${}^{\mathrm{ex}}G$ is the excess Gibbs energy of mixing and is defined as follows:

$$ {}^{\mathrm{ex}}G = y_{\mathrm{Nb}}^{\mathrm{I}} y_{\mathrm{Ti}}^{\mathrm{I}} \sum_{X_\mathrm{II}=\mathrm{O,Va}} y_{X_\mathrm{II}}^{\mathrm{II}} \sum_{n} {}^{(n)}L_{\mathrm{Nb,Ti}:X_\mathrm{II}}^{A} (y_{\mathrm{Nb}}^{\mathrm{I}} - y_{\mathrm{Ti}}^{\mathrm{I}})^n + y_{\mathrm{O}}^{\mathrm{II}} y_{\mathrm{Va}}^{\mathrm{II}} \sum_{X_\mathrm{I}=\mathrm{Nb,Ti}} y_{X_\mathrm{I}}^{\mathrm{I}} \sum_{n} {}^{(n)}L_{X_\mathrm{I}:\mathrm{O,Va}}^{A} (y_{\mathrm{O}}^{\mathrm{II}} - y_{\mathrm{Va}}^{\mathrm{II}})^n, \tag{2}$$

where ${}^{(n)}L_{\mathrm{Nb,Ti}:X_\mathrm{II}}^{A}$ and ${}^{(n)}L_{X_\mathrm{I}:\mathrm{O,Va}}^{A}$ are interaction parameters and the site fraction, $y_{X_m}^m$, is related to the mole fraction, x_X, by the following equations:

$$y_{\mathrm{Nb}}^{\mathrm{I}} = \frac{x_{\mathrm{Nb}}}{1 - x_{\mathrm{O}}}, \tag{3}$$

$$y_{\mathrm{Ti}}^{\mathrm{I}} = \frac{x_{\mathrm{Ti}}}{1 - x_{\mathrm{O}}}, \tag{4}$$

$$y_{\mathrm{O}}^{\mathrm{II}} = \frac{x_{\mathrm{O}}}{\frac{q^A}{p^A}(1 - x_{\mathrm{O}})}, \tag{5}$$

$$y_{\mathrm{Va}}^{\mathrm{II}} = 1 - y_{\mathrm{O}}^{\mathrm{II}}. \tag{6}$$

The thermodynamic parameters of each phase are summarized in Table 1 [17–21].

2.2. Phase-field model

The nanodomains are presumed to exhibit metastable structures that are approximately halfway between β and α" structure; however, they are regarded as the α" phase for simplicity. To distinguish between the β and α" phases, a phase-field order parameter, $\phi(\mathbf{r},t)$, which can be regarded as the probability of finding the α" phase at $\mathbf{r}$ and t, is defined as a field variable; herein, $\phi(\mathbf{r},t)$ is equal to unity if $\mathbf{r}$ points the α" phase and is zero if $\mathbf{r}$ points the β phase. The concentration field of each component X, denoted as $z_X(\mathbf{r},t)$ (X = Nb, Ti, and O), is also regarded as a field variable. $z_X(\mathbf{r},t)$ is determined from x_X, as follows [22]: