β -Phase Instability in Binary Ti- x Nb Biomaterial Single Crystals

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The ω -phase transformation and β -phase stability in Ti- x Nb ($28 \leq x \leq 40$ at%) single crystals were investigated using electrical resistivity measurements, transmission electron microscopy (TEM) observations, and specific heat measurements. The crystal for $x = 28$ exhibits distinct anomalous negative temperature dependence of the resistivity coefficient and thermal hysteresis accompanied by the presence of the athermal ω -phase and β -phase lattice modulation. Although the crystal for $x = 30$ appears in the β -phase lattice modulation, it does not exhibit a clear negative temperature dependence of the resistivity coefficient or the athermal ω -phase. The crystal of $x = 30$ also shows a relatively high absolute value of resistivity at 15 K among the crystals for $28 \leq x \leq 40$ and a low Debye temperature in a normal conductive state. The crystal for $x = 30$ that shows the lattice modulation, high resistivity, and low β -phase Debye temperature correspond to the low stability of the β -phase. Moreover, the stability strongly depends on the Nb content of the binary Ti-Nb crystal. [doi:10.2320/matertrans.MC201202]

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1. Introduction

β Ti-Nb-based alloys with the body-centered cubic (bcc) structure have recently received a considerable attention as promising candidates for biomaterials because they exhibit good biocompatibility, low Young's moduli, superior strength and shape memory effect among other physical properties. In particular, it is necessary to reduce the Young's modulus and to control the mechanical properties of biomaterials for applications such as artificial joints and dental implants.¹⁾ The former is necessary to prevent bone degradation and absorption.²⁻⁴⁾ This phenomenon is the so-called "stress shielding" caused by a difference between the Young's modulus of metallic implants and that of natural human bone. The latter is achieved by improving the microstructure and by changing the constituent phases (such as the α -, β - and/or martensite phases) of β -phase Ti-based alloys.⁵⁾ Thus, numerous β -phase Ti-Nb-based alloys with low Young's moduli and suitable mechanical properties have been developed to date, for example, Ti-Nb,^{6,7)} Ti-Nb-Al,⁸⁾ Ti-Nb-Si,⁹⁾ Ti-Nb-Sn,¹⁰⁻¹²⁾ Ti-Nb-Mo,¹³⁾ Ti-Nb-Ta,¹⁴⁾ Ti-Nb-Zr,¹⁵⁾ Ti-Nb-Zr-Sn¹⁶⁾ and Ti-Nb-Ta-Zr alloys.^{17,18)}

Recently, our group investigated the elastic stiffness and elastic anisotropy of some single β -phase Ti alloys of Ti-Nb-Ta-Zr and Ti-Mo-Zr-Al using their single crystals.¹⁹⁻²¹⁾ We found that elastic softening occurs and that the Young's modulus along the $\langle 100 \rangle$ direction is the lowest in all crystallographic orientations for the β -phase Ti single crystals. The Young's modulus along the $\langle 100 \rangle$ direction in the β -phase Ti alloys is similar to that of human bone. Furthermore, we proposed that suppressing the formation of the ω -phase and decreasing the electron-atom (e/a) ratio are important criteria for reducing the Young's modulus of β -phase Ti alloys. The e/a ratio is the average number of valence electrons per atom in a free atomic configuration.

A reduced Young's modulus is caused by β -phase instability, resulting in lattice softening corresponding to low shear modulus, c' .²²⁾ It is necessary to understand the β -

phase stability in order to further develop β -phase Ti alloys because it possibly affects their mechanical properties.

Lattice softening along the $\{110\}$ $\langle 110 \rangle$ direction is an important β -phase phenomenon. Moreover, lattice modulation occurs in the β -phase. Lattice modulation is caused by a transverse wave consistent with the displacement of atoms in the $[110]$ direction, which is common in Ti-Nb-based alloys with low reported e/a , such as (Ti-23Nb)-1.0O alloy ($e/a = 4.23$)²³⁾ and binary Ti-29Nb alloy ($e/a = 4.29$).²⁴⁾ In addition, the intensity of diffuse satellites is characteristic of changes in lattice modulation due to uniaxial stress.²³⁾ However, the detailed relation between the lattice modulation and the β -phase stability has not necessarily been clearly understood yet. The purposes of this study, therefore, are to understand the relation between the lattice modulation and/or ω -phase transformation and the physical properties (i.e., the electrical resistivity and specific heat) of the binary Ti- x Nb single crystals and to discuss the relation between the existence of lattice modulation and phase stability for the β -phase of Ti- x Nb single crystals for ($28 \leq x \leq 40$) that exhibit e/a ratios between 4.28 and 4.40.

2. Experimental Procedure

Ingots of Ti- x Nb alloys ($x = 28, 30, 32, 34, 36$ and 40 at%) were prepared using arc melting on a water cooled copper hearth in a high purity argon gas atmosphere. These ingots were re-melted at least five times. Single crystal rods of these alloys were grown using an optical floating zone apparatus (Canon machinery: SCI-MDH-20020) at a crystal growth rate of 2.5 mm/h under a high purity argon gas flow. It was confirmed that the O content in all the single crystals are below 0.25 at%. And, the analyzed chemical composition of Ti-28Nb crystal is, for example, Ti-27.92Nb-0.22O-0.12N (in at%). Specimens for all measurements were cut from the single crystal rods and were subsequently annealed at 1273 K for 1 h and then quenched into ice water. The oxidized surface layer was removed using electropolishing in a solution of 6 vol% perchloric acid, 35 vol% butanol and 59 vol% methanol at about 230 K. Each alloy is hereinafter

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Fig. 1 Temperature dependence of electrical resistivity (ρ) for Ti-xNb ($28 \leq x \leq 40$) single crystals.

referred to by its Nb content, e.g., Ti-28at% Nb is represented by 28Nb. The e/a was calculated using the chemical compositions of Ti and Nb on the basis of the electron configurations of Ti ($[\text{Ar}]3d^24s^2$) and Nb ($[\text{Kr}]4d^45s^1$). For example, an e/a of 4.3 is expected for 30Nb alloys. Electrical resistivity (ρ) was measured using a standard four probe method with a cooling and heating rate of 1 K/min. The resistivity of all specimens does not exhibit orientation dependence, but the $[\bar{1}49]$ orientation in single crystals where the Schmid factor of the $(\bar{1}01)$ $[111]$ primary slip system has a maximum value of 0.5 was selected to analyze electrical resistivity in order to facilitate the comparison with that in the specimens for future plastic deformation experiments by using single crystals. Plastic deformation is expected to promote the phase transformation in the crystals.

Thin foils for TEM observation were prepared using electropolishing in an acidic electrolyte. TEM observation was performed using a JEM 3010 operated at 300 kV. Specific heat was measured using a relaxation method in the physical property measurement system (PPMS) from

Quantum Design. During each specific heat measurement, a specimen was heated to 2% of its absolute temperature, and the heat capacity was calculated based on the relaxation time during thermal conduction cooling.

3. Results

3.1 Electrical resistivity

Figure 1 shows graphs representing the change in the electrical resistivity of the Ti-xNb single crystals measured during cooling and heating. The graph for the resistivity of the 28Nb crystal measured during cooling exhibits a local minimum at $T_{\min} = 225$ K, as indicated with an arrow, and exhibits an anomalous negative temperature coefficient (NTC) below 225 K. An NTC was observed for some β -phase Ti alloys.^{24–28} The appearance of an NTC is interpreted as the growth of the athermal ω -phase and the appearance of lattice modulation.^{24,27} The resistivity of the 28Nb crystal decreases again at 100 K, as indicated with a double arrow. The resistivity of the 28Nb crystal also exhibits

Fig. 2 Change in superconductive transition temperature (T_c) with increasing Nb content in Ti- x Nb ($28 \leq x \leq 40$) single crystals.

a thermal hysteresis between cooling and heating caused by the athermal ω -phase transformation because it is the first transformation. The resistivity of the 30Nb crystal does not strongly depend on temperatures in the range 100–200 K. These results are consistent with those of previous studies.^{24,25} Concerning the 32Nb, 34Nb, 36Nb and 40Nb crystals, neither remarkable changes in the temperature coefficient nor thermal hysteresis of resistivity were found, as shown in Fig. 1. The abrupt decrease in resistivity below 10 K observed for all the crystals is due to a superconductive transition. The superconductive transition temperature, T_c , of the crystals for $x \geq 30$ increases with increasing Nb content, as shown in Fig. 2. This relation does not hold for the 28Nb crystal because of the ω -phase precipitate in the 28Nb crystal.²⁴ The resistivity measurements suggest athermal ω -phase formation is suppressed at around 28Nb because almost all the ω -phase is produced at room temperature, as discussed later.

3.2 Lattice modulation in electron diffraction patterns

The selected-area electron diffractions (SAEDs) for the 28Nb and 30Nb crystals were observed using TEM to determine whether athermal ω -phase formation and lattice modulation had occurred. Figures 3(a) and 3(b) show the typical selected area diffraction patterns (SADPs) for the 28Nb and 30Nb crystals, respectively, taken with a beam

direction of $[113]$ at room temperature. The SADPs of the 28Nb crystal basically show the presence of the β -phase and additional slight streaks along the $\langle 112 \rangle^*$ direction, where the asterisk (*) indicates orientation in a reciprocal lattice space, as shown in Fig. 3(a). This result is consistent with that in a previous report²⁴) and indicates that a small volume of the athermal ω -phase is embedded in the β -phase matrix (photo is not shown here) at room temperature. In a previous study, the intensity of the streaks depends on the temperature during *in-situ* TEM observation, and diffuse satellites appears in the SADP for the 28Nb crystal at $g_\beta + 2/3\langle \zeta\zeta\zeta \rangle^*$ and $g_\beta + 4/3\langle \zeta\zeta\zeta \rangle^*$, where g_β is the β -phase reciprocal lattice vector.^{24,29} Streaks along the $\langle 110 \rangle^*$ direction are also observed in the SADP for 28Nb measured at room temperature. These streaks are caused by lattice modulation²⁴) associated with a transverse wave, consistent with atom displacement in the $\langle 110 \rangle$ direction.^{23,24} Tahara *et al.* reported that similar streaks along the $\langle 110 \rangle^*$ direction and diffuse satellites appeared at $g_\beta + 1/2\langle \zeta\zeta 0 \rangle^*$ in the SADP for the Ti-Nb-O alloy.²³) They also observed the β -phase lattice modulation morphologies, which are referred to as “nanodomains”, and suggested that this lattice modulation is caused by the distributed oxygen atoms and the related local strain fields. However, the lattice modulation appears in both Ti-Nb and Ti-Nb-O alloys. This suggests that the lattice modulation is related to not only the existence of oxygen but also β -phase stability.

The diffraction pattern for the 30Nb crystal prepared in this study also shows the β -phase diffraction and slight streaks along the $\langle 110 \rangle^*$ direction but not streaks along the $\langle 112 \rangle^*$ direction, as shown in Fig. 3(b). To the best of our knowledge, this is the first report to find only lattice modulation in the 30Nb crystal. The streaks along the $\langle 110 \rangle^*$ direction were also observed in the diffraction pattern for the 30Nb crystal when the beam direction was $[001]$, as shown in Fig. 3(c). This strongly suggests that although the athermal ω -phase and lattice β -phase modulation occur in the 28Nb crystal, only β -phase lattice modulation appears in the 30Nb crystal at room temperature. From the resistivity analysis results, athermal ω -phase formation is also suppressed in the 30Nb crystal at low temperatures, which suggests that the lattice modulation in the 30Nb crystal is temperature dependent and possibly exhibits very weak diffuse satellites in the SADP at the $g_\beta + 1/2\langle \zeta\zeta 0 \rangle^*$ position.

Fig. 3 SAEDs generated at room temperature for Ti- x Nb single crystals. (a) Beam direction $// [113]$, 28Nb; (b) beam direction $// [113]$, 30Nb; and (c) beam direction $// [001]$, 30Nb.

Fig. 4 Temperature dependence of specific heat (C_p) for 30Nb single crystal.

Fig. 5 Temperature dependence of specific heat (C_p) for 30Nb single crystal in low-temperature region.

3.3 Stability of β -phase matrix

In order to further understand the β -phase stability with regard to lattice modulation, the specific heat (C_p) of the 30Nb crystal was measured, and the temperature dependence of C_p is shown in Fig. 4. A peak corresponding to the superconductivity transition is observed below 10 K in this curve in Fig. 5.³⁰⁾ In order to discuss the β -phase stability with regard to lattice modulation, C_p/T is plotted as a function of T^2 above T_c , and a linear relation is obtained, as shown in Fig. 6. The Debye temperature, Θ_D , of the β -phase was calculated on the basis of the slope on the basis of the slope (β) by using the following equation:

$$\beta = \frac{12\pi^4 N_A k_B}{5\Theta_D^3}, \quad (1)$$

where N_A is the Avogadro's number and k_B is the Boltzmann constant. The Θ_D value of the β -phase was 228 K and 231 K for the 30Nb and 40Nb crystals, respectively. These values are smaller than that of the 50Nb alloy (= 235 K) and 75Nb alloy (= 255 K).³⁰⁾ It should be noted that the Θ_D value of the β -phase decreases with decreasing Nb content, meaning that the β -phase lattice in Ti-xNb crystals softens with decreasing Nb content and corresponding e/a . For a Ti-Nb binary system, the Θ_D of the 30Nb crystal is located at approximately a local minimum, resulting in β -phase softening.

Fig. 6 Relation between C_p/T and T^2 for 30Nb single crystal in low-temperature region above T_c .

Fig. 7 Change in electrical resistivity at 15 K (ρ_{15K}) with increasing Nb content.

From the viewpoint of the Young's modulus, it has previously been reported that the shear modulus, c' , which is closely related to the softening mode of $\{110\}$ $\langle 110 \rangle$, monotonically decreases with decreasing e/a ¹⁹⁻²¹⁾ and that c' for the 30Nb crystal was very low.⁶⁾ Therefore, the β -phase lattice modulation in the 30Nb crystal has low β -phase stability, which is related to lattice softening.

High resistivity can also be observed at 15 K in the resistivity plots for the 28Nb and 30Nb crystals, as shown in Fig. 7. That is, considering that Nb atoms will act as an obstacle for conduction electrons, the resistivity, ρ_{15K} , should increase with increasing Nb content in the β -phase. However, this relation does not hold for $28 \leq x \leq 40$. This behavior indicates that the 30Nb crystal lattice was unstable without the presence of the athermal ω -phase and that the β -phase lattice is stable with increasing e/a for $30 < x \leq 40$, while the athermal ω -phase that appeared in the 28Nb crystal increases the resistivity at 15 K. The big gap in ρ_{15K} from 30Nb to 32Nb may be due to the abrupt increase in β -phase stability.

The electron specific heat coefficient, γ , was also obtained as the C_p/T^2 -intercept. The γ of the 30Nb crystal was 10.7 ($\text{mJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$), higher than that for the bcc-structured pure

Nb. A High γ suggests that electron–phonon interaction is strong in the unstable 30Nb β -phase and that the lattice is strongly affected by electronic structure. Similarly low Θ_D and high γ values have previously been reported for Ti–Ni-based shape memory alloys with lattice modulations caused by anomalous electronic structure.^{31–33)}

In summary, β -phase stability in Ti– x Nb alloys strongly depends on Nb content, resulting in high electrical resistivity and low Debye temperature. Further study on β -phase single crystals of Ti– x Nb alloys is now in progress to understand the relationship between the β -phase stability due to the electronic structure and the mechanical properties of these alloys.

4. Conclusion

The close relation between the β -phase stability and the physical properties of Ti– x Nb single crystals were investigated using electrical resistivity measurements, TEM observations, and specific heat measurements. The resistivity of the 28Nb alloy exhibits an anomalous negative temperature coefficient and a thermal hysteresis related to athermal ω -phase precipitation in the electrical resistivity in addition to β -matrix lattice modulation. The crystals for $x \geq 30$, on the other hand, exhibit neither a clear negative temperature dependence nor thermal hysteresis in their respective resistivity curves. The 30Nb crystal β -phase exhibits lattice modulation and a low Debye temperature. In addition, the resistivity of 30Nb at 15 K was higher than that of the alloys for $x > 30$, corresponding to the relatively low β -phase stability in 30Nb.

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