Origin of ultralow Young's modulus in a metastable β -type Ti-33Nb-4Sn alloy

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Abstract

Although there is difficulty in growing a Ti-33Nb-4Sn single crystal due to its ultralow β -phase stability, the single-crystal elastic constants of metastable β -type Ti-33Nb-4Sn (wt.%) alloy were extracted successfully from its polycrystal by in-situ synchrotron X-ray diffraction technique, to clarify the origin of the ultralow Young's modulus in its polycrystal. It is indicated that compared to binary TiCr, TiV and TiNb alloys, the Ti-33Nb-4Sn alloy possesses slightly lower β -phase stability with respect to $\{110\}\langle 1\bar{1}0\rangle$ shear (i.e., C') but much lower β -phase stability regarding to $\{001\}\langle 100\rangle$ shear (i.e., C_{44}). An analysis by the Hill approximation suggests that the ultralow isotropic polycrystalline Young's modulus (E_H) of Ti-33Nb-4Sn alloy originates from the extremely low shear modulus C_{44} as well as the relatively low C' . This indicates that in addition to C' , C_{44} has a significant contribution to the Young's modulus of polycrystal, which challenges a conventional understanding that the Young's modulus of β -type Ti alloys is predominantly determined by C' .

Keywords : Metastable β Ti alloy; Elastic behavior; Young's modulus; In-situ synchrotron X-ray diffraction.

1. Introduction

Titanium and its alloys have been widely used for hard tissue replacement materials due to their excellent biocompatibility, high corrosion resistance and good mechanical properties, especially relatively low Young's modulus (Geetha et al., 2009; Hao et al., 2007; Saito et al., 2003). Among the mechanical properties necessary for implant materials, Young's modulus is generally considered to be of dominant importance, because implant failure can occur due to the mismatch in Young's modulus between the implant materials and nature human bone (Geetha et al., 2009; Ho et al., 1999). As is well known, the most widely used Ti implant material, ($\alpha+\beta$) type Ti-6Al-4V, exhibits a Young's modulus of ~110 GPa, which is much higher than that of human bone (~30 GPa) (Geetha et al., 2009). Thus, in the past few decades, much research effort has been devoted to the development of metastable β -type Ti alloys with lower Young's modulus, such as Ti-Mo (Oliveira et al., 2007), Ti-Nb-Ta-Zr (Morris et al., 2010), Ti-Nb-Zr-Sn (Hao et al., 2007), etc. Currently, β -type Ti alloys designed for hard tissue replacement have Young's moduli in the range of 50~80 GPa, which still cannot match perfectly with human bone. Quite recently, a metastable β -type Ti-33Nb-4Sn (wt. %) alloy, consisting entirely of non-cytotoxic elements, was fabricated by the present authors for biomedical applications (Guo et al., 2015). Upon cold deformation plus short-time annealing, this alloy can show an ultralow tensile Young's modulus of 36 GPa. This level of Young's modulus is the lowest ever recorded for the currently available biomedical Ti alloys, and is only ~6 GPa higher than that of human bone (Guo et al., 2015). However, the origin of the ultralow Young's modulus in the Ti-33Nb-4Sn alloy has not yet been clarified in detail, although an in-depth understanding of this issue may provide a clear design concept for further decreasing the Young's modulus in metastable β -type

Ti alloys.

Previous investigations showed that the Young's moduli of polycrystalline body-centered cubic (bcc) metals are closely related to their single-crystal elastic constants (SECs), i.e., C_{11} , C_{12} , and C_{44} (Hill, 1952). As far as β -type Ti alloys with bcc structure, shear modulus C' , which is equivalent to $(C_{11}-C_{12})/2$ and represents the stability of β phase with respect to $\{110\}\langle\bar{1}\bar{1}0\rangle$ shear, was once considered as the most important factor controlling the Young's modulus of polycrystal (Zener, 1947), because the Young's modulus decreases with decreasing the β -phase stability (Abdel-Hady et al., 2006; Guo et al., 2014). Thus, previous studies were mainly focused on clarifying the key role of shear modulus C' on the Young's moduli of polycrystalline β -phase Ti alloys (Hu et al., 2008; Obbard et al., 2011; Tegner et al., 2012). Actually, from the viewpoint of crystallography, in addition to C' , C_{44} should also be considered as a key parameter for evaluating β -phase stability, since C_{44} represents **resistance to** $\{001\}\langle 100\rangle$ shear (Otsuka et al., 2005), being similar to C' corresponding to $\{110\}\langle\bar{1}\bar{1}0\rangle$ shear. Therefore, the possible contribution of C_{44} to Young's modulus of metastable β -type Ti alloys should be taken into account.

Generally, the elastic constants of β -type Ti alloys, i.e., C_{11} , C_{12} , and C_{44} , can be obtained by measuring their corresponding single crystals using resonant ultrasound spectroscopy and/or electromagnetic acoustic resonance (Hermann et al., 2012). However, although many Ti single crystals have been grown successfully in binary β -type Ti alloys (Ahlberg et al., 1978; Hermann et al., 2012), it is still difficult or even impossible to grow single crystals for ternary or quaternary β -type Ti alloys, especially for Ti-33Nb-4Sn alloy. The difficulties in growing a Ti-33Nb-4Sn single crystal lie in the following two aspects: on one hand, the Ti-33Nb-4Sn alloy exhibits a mixture of β - and α' - phases in the solution treated state due to its ultralow β -phase

1 stability caused by low content of β stabilizers; on the other hand, severe cold
2 deformation plus short-time annealing is necessary for Ti-33Nb-4Sn alloy to achieve
3 ultralow Young's modulus (Guo et al., 2015).
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7 Previous studies have revealed that the valence electrons per atom (e/a ratio)
8 have a dominant influence on the elastic constants (Lee et al., 2012; Tane et al., 2008).
9 The e/a ratio is the valence based on the total d plus s electrons in the free atom
10 configuration and corresponds to the position of Fermi level (Ikehata et al., 2004).
11 Generally speaking, the e/a ratio is determined by the type and content of β stabilizers
12 and increases with the increasing amount of β stabilizers (Hao et al., 2007). In binary
13 β -type Ti alloys, shear modulus C' and bulk modulus B decrease with decreasing e/a
14 ratio while the shear modulus C_{44} keeps almost unchanged, thus it is obvious that the
15 Young's modulus can be reduced by decreasing e/a ratio (Tane et al., 2010). Therefore,
16 it is helpful to investigate the relationship between the SECs and e/a ratio so as to
17 elucidate the cause of low Young's modulus and finally reduce the Young's modulus
18 of β -type Ti alloys. In the study, an attempt was made to extract the SECs of
19 metastable β -type Ti-33Nb-4Sn alloy from its polycrystal by in-situ synchrotron
20 X-ray diffraction technique and Eshelby-Kroner-Kneer elastoplastic self-consistent
21 (EPSC) model (Talling et al., 2008). Compared with the dependence of SECs on e/a
22 ratio in binary β -type alloys, the origin of ultralow Young's modulus in a metastable
23 β -type Ti-33Nb-4Sn alloy was discussed.
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48 **2. Experimental procedure**

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50 An ingot with a nominal composition of Ti-33Nb-4Sn (wt. %) was arc melted in
51 an argon atmosphere using high purity Ti (99.99%), Nb (99.95%) and Sn (99.95%).
52 The ingot was homogenized, forged and then solution treated at 1073 K for 1 hour,
53 followed by quenching into water (~298 K). The test samples that were spark cut from
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the solution treated billet will be denoted as ST specimens henceforth. The ST billet was cold rolled at a thickness reduction of 87%, and then annealed at 673 K for 20 minutes followed by quenching into water. These resultant specimens will be referred to as CRA specimens henceforth. A more detailed description of fabricating Ti-33Nb-4Sn alloy can be seen in our previous reference (Guo et al., 2015).

X-ray diffraction (XRD) measurements were performed by a Rigaku D/max 2550 diffractometer with Cu K α radiation. The texture of β phase was also characterized by XRD and the data were dealt with using preferred orientation package from Los Alamos National Laboratory. Microstructure observation was conducted on a FEI Tecnai F20 transmission electron microscope (TEM). Uniaxial tensile test was performed along the rolling direction, using an Instron-8801 testing system at a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$. The in-situ synchrotron X-ray experiments were conducted on the 11-ID-C beam-line of Advanced Photon Source at Argonne National Laboratory, and the data were obtained from a $\pm 5^\circ$ region for grains with crystal planes perpendicular to the loading direction.

3. Results and discussion

The XRD patterns of ST and CRA Ti-33Nb-4Sn alloys are shown in Fig. 1a. A mixture of β - and α'' - phases was observed in the ST specimen, indicating that a martensitic transformation from β (bcc) to orthorhombic α'' occurs upon quenching. This is attributed to the low β -phase stability of the present alloy caused by its low content of β stabilizers. After cold rolling plus annealing, α'' martensite was transformed reversibly to β phase, and the β phase was almost completely retained at room temperature with a few α precipitates. The same results of phase constituents for the ST and CRA specimens were revealed by TEM technique, as shown in Fig. 1b and Fig. 1c, respectively. These results from XRD and TEM suggest that the β to α''

1 martensite is effectively retarded by cold rolling plus subsequent annealing treatment.
2 Our previous experimental study has demonstrated that the retard of the martensitic
3 transformation in Ti-33Nb-4Sn alloy is due to high density of dislocations and grain
4 boundaries induced by cold rolling plus annealing (Guo et al., 2015), as shown by the
5 TEM image in Fig. 1c. Fig. 1d shows the tensile stress-strain curves of ST and CRA
6 Ti-33Nb-4Sn alloys. It is clear that although the ST alloy exhibits low Young's
7 modulus, it is not suitable for biomedical applications due to its relatively low yield
8 strength (~107 MPa) stemming from stress-induced $\beta \rightarrow \alpha''$ martensitic transformation.
9 Upon cold rolling plus annealing, the Ti-33Nb-4Sn alloy was remarkably
10 strengthened, with high yield strength of ~763 MPa and ultimate tensile strength of
11 ~853 MPa. More importantly, the CRA alloy exhibited an ultralow tensile Young's
12 modulus of ~36 GPa (vs. ~30 GPa for human bone).

13 In order to clarify the origin of ultralow Young's modulus in Ti-33Nb-4Sn alloy,
14 the SECs of CRA Ti-33Nb-4Sn alloy were extracted by in-situ synchrotron X-ray
15 diffraction technique and EPSC model. Fig. 2 shows the plots of macrostress for
16 $\{110\}_\beta$, $\{200\}_\beta$, $\{211\}_\beta$, and $\{310\}_\beta$ planes perpendicular to the loading direction
17 versus lattice strain. From these curves, the diffraction elastic constants (DECs) of the
18 $\{110\}_\beta$, $\{200\}_\beta$, $\{211\}_\beta$, and $\{310\}_\beta$ planes can be measured by determining the
19 incipient slope of the macrostress-lattice strain curves. On the other hand, the DECs
20 can also be obtained by running EPSC model over and over again using different
21 SECs, i.e., shear modulus $C'=(C_{11}-C_{12})/2$, shear modulus C_{44} and bulk modulus
22 $B=(C_{11}+2C_{12})/3$, as input parameters. The SECs input parameters, which make the
23 weighted sum of squared residuals (WSSR) between the experimental and calculated
24 DECs reach the minimum value, will be eventually identified as the SECs of CRA
25 Ti-33Nb-4Sn specimen.

During the process of running EPSC model, the texture data of CRA Ti-33Nb-4Sn alloy were also inputted into this model for accurate calculation. Additionally, the B value was fixed at a constant value during the running of EPSC model, since the values of C' and C₄₄ with minimum WSSR are insensitive to B value, when the B value exceeds 100 GPa (see the Table. S1 in the supplemental information). It is well known that most of experimental values of B vary within the range of 100~140 GPa in β -phase Ti alloys, and that B increases monotonically with an increase in e/a ratio (i.e. average valence electron number), obeying a linear relationship (Boyer et al., 1994; Tane et al., 2010). Therefore, the B value for Ti-33Nb-4Sn alloy was fixed at 110 GPa by reference to binary Ti-9.36Cr (at. %, e/a=4.19) alloy which has the similar e/a ratio with the present alloy (e/a=4.20) (Fisher et al., 1970; Tane et al., 2010). For the given B value of 110 GPa, a set of optimum C' and C₄₄ can be obtained, making the WSSR between the experimental and calculated DEC's reach the minimum value. The optimum SEC's (GPa) that give the best fit to DEC's and anisotropy factor A (dimensionless) for CRA Ti-33Nb-4Sn alloy are shown in Table 1.

The experimental and calculated DEC's of CRA Ti-33Nb-4Sn alloy are listed in Table 2, where the experimental DEC's were measured from the macrostress-lattice strain curves in Fig. 2, while the calculated DEC's were obtained by EPSC model using the optimum C', C₄₄ and B as input parameters. One can see that the calculated DEC's for {110} _{β} , {200} _{β} , {211} _{β} , and {310} _{β} were in very good agreement with the corresponding experimental DEC's, verifying that our EPSC modeling is valid and reliable. This also suggests that the SEC's of Ti-33Nb-4Sn alloy can be successfully extracted from its polycrystal by in-situ synchrotron X-ray diffraction technique and EPSC model.

Fig. 3a and Fig. 3b show the shear moduli C' and C_{44} of CRA Ti-33Nb-4Sn alloy, along with those of β -type Ti-Cr (Fisher et al., 1970), Ti-V (Katahara et al., 1979) and Ti-Nb (Reid et al., 1973) single crystals as a function of e/a ratio, respectively. It can be seen from Fig. 3a that in binary β -phase Ti alloys, the shear moduli C' decreases with decreasing e/a ratio, obeying an empirical correlation between the C' and e/a as follow (Fisher et al., 1970):

$$C' = 1.391 \times (e/a - 2)^{3.34} \text{ (GPa)} \quad (1),$$

where Eq.(1) is valid when $4.15 < e/a \leq 6$. At a e/a ratio of 4.20, the C' of the Ti-33Nb-4Sn alloy was lower than those of β -type Ti-Cr, Ti-V and Ti-Nb alloys with the similar e/a ratio, indicating that the Ti-33Nb-4Sn alloy possesses lower β -phase stability regarding to $\{110\}\langle\bar{1}\bar{1}0\rangle$ shear than Ti-Cr, Ti-V and Ti-Nb alloy. Unlike C' determined by e/a , C_{44} was insensitive to the e/a ratio and kept almost constant in binary β -type Ti alloys, as shown in Fig. 3b. Here, an important point to note is that the Ti-33Nb-4Sn alloy exhibited a C_{44} of 22.4 GPa, significantly lower than those of β -type Ti-Cr, Ti-V and Ti-Nb alloys. This result suggests that compared to binary β -type Ti alloys, the present alloy possesses much lower β -phase stability with respect to $\{001\}\langle100\rangle$ shear. The extremely low C_{44} of the Ti-33Nb-4Sn alloy results in lower anisotropy factor (A , which is equivalent to C_{44}/C') than those of the binary alloys with the similar e/a ratio (see Fig. 3c), revealing that the difference in β -phase stability regarding to $\{001\}\langle100\rangle$ and $\{110\}\langle\bar{1}\bar{1}0\rangle$ shear is not significant in Ti-33Nb-4Sn alloy. According to the above results shown in Fig. 3a~c, it can be concluded that in comparison to binary β -type Ti-Cr, Ti-V and Ti-Nb alloys, the Ti-33Nb-4Sn alloy possesses lower β -phase stability with respect to both $\{110\}\langle\bar{1}\bar{1}0\rangle$ and $\{001\}\langle100\rangle$ shear and **lower anisotropy factor**. Thus, it is reasonable to expect

that the Ti-33Nb-4Sn alloy exhibits lower Young's modulus than those of binary β -type alloys.

Based on the assumption that strain and stress are uniform throughout polycrystalline materials during elastic deformation, the Young's moduli (E_H) of isotropic bcc metals can be calculated from their SECs by using the Hill approximation (Hill, 1952):

$$E_H = \frac{1}{2} \left(\frac{9}{1/B + 15/(2C' + 3C_{44})} + \frac{5}{5/(9B) + 2/(3C') + 1/C_{44}} \right) \quad (2)$$

, where C' has the greatest degree of contribution to E_H , C_{44} has a slightly smaller degree of contribution to E_H than C' , and the contribution of B is the smallest among all the SECs (Fisher et al., 1970; Hill, 1952). The E_H of Ti-Cr (Fisher et al., 1970), Ti-V (Katahara et al., 1979), Ti-Nb (Reid et al., 1973) and Ti-33Nb-4Sn alloys was plotted as a function of e/a ratio in Fig. 3d. The E_H of binary β -type TiCr, TiV and TiNb alloys was controlled by C' and increased monotonically with an increase in e/a ratio, because the C_{44} of binary alloys is independent on e/a ratio and remains nearly constant. Compared to binary Ti alloys, the Ti-33Nb-4Sn polycrystal exhibited much lower E_H due to its lower C' and much lower C_{44} .

Zener et al. first proposed that shear modulus C' , which represents the resistance to $\{110\}\langle 1\bar{1}0 \rangle$ shear and is controlled by e/a ratio, can be employed to evaluate the stability of bcc structure (Zener, 1947). Early studies showed that the Young's modulus of β -type Ti polycrystals decreases with decreasing C' , accompanied by a decrease in β -phase stability (Guo et al., 2014; Hu et al., 2008; Obbard et al., 2011; Tegner et al., 2012; Zener, 1947). Therefore, C' was once considered as the only parameter evaluating the β -phase (bcc) stability, especially in binary β -type Ti alloys. However, it was found recently that in TiNi based alloys with bcc structure, both C'

and C_{44} are important parameters evaluating the stability of bcc structure, and that they are both quite low when the bcc loses its stability and transforms to monoclinic B19' or orthorhombic B19 (Otsuka et al., 2005). Therefore, C' and C_{44} , which corresponds to the resistance to $\{110\}\langle\bar{1}\bar{1}0\rangle$ and $\{001\}\langle100\rangle$ shear, respectively, should both be considered as important parameters to evaluate the stability of bcc. In the case of Ti-33Nb-4Sn alloy, from the viewpoint of composition design, the content of β stabilizers (i.e., e/a ratio) is lowered purposefully so as to achieve low modulus. As a result, a martensitic transformation from β phase (corresponding to bcc phase in TiNi alloys) to orthorhombic α'' (corresponding to orthorhombic B19 in TiNi alloys) occurs during quenching due to its low β stability. Upon subsequent cold rolling and annealing, the β phase still remains low β stability with respect to $\{110\}\langle\bar{1}\bar{1}0\rangle$ and especially to $\{001\}\langle100\rangle$ shear, as evidenced by its low C' and extremely low C_{44} shown in Fig. 3, although the β phase survives against α'' martensitic transformation at room temperature (Fig. 1). These results suggest that with the assistance of appropriate thermo-mechanical treatment (i.e., cold rolling plus short-time annealing), low β -phase stability with respect to resistance to $\{110\}\langle\bar{1}\bar{1}0\rangle$ (i.e., C') and especially for $\{001\}\langle100\rangle$ shear (i.e., C_{44}) can be obtained, giving rise to an ultralow isotropic polycrystalline Young's modulus in Ti-33Nb-4Sn alloy. Also, our results reveal that in addition to C' , C_{44} has a significant contribution to the E_H of polycrystal, which is different from the conventional cognition that the Young's modulus of β -type Ti alloys is predominantly determined by C' (Fisher et al., 1970; Katahara et al., 1979; Reid et al., 1973; Zener, 1947).

4. Conclusion

In summary, we extracted successfully the SECs of metastable β -type

1 Ti-33Nb-4Sn (wt.%) alloy from its polycrystal by in-situ synchrotron X-ray
2 diffraction technique and EPSC model. In comparison to binary TiCr, TiV and TiNb
3 alloys, the Ti-33Nb-4Sn alloy exhibits slightly lower β -phase stability with respect to
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7 $\{110\}\langle 1\bar{1}0\rangle$ shear (i.e., C'), but much lower β -phase stability regarding to $\{001\}\langle 100\rangle$
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9 shear (i.e., C_{44}). Further analysis by the Hill approximation shows that in addition to
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11 C', the extremely low shear modulus C_{44} plays a key role in realizing the ultralow
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13 Young's modulus of Ti-33Nb-4Sn polycrystal. This result suggests decreasing C_{44} by
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15 appropriate thermo-mechanical treatment might be an effective approach for β -type Ti
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17 alloys to obtain ultralow Young's modulus comparable with that of human bone,
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19 which may benefit designs of novel β -type Ti alloys for biomedical applications.
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Figure and Table captions:

Figure 1. XRD patterns of ST and CRA Ti-33Nb-4Sn specimens (a), bright-field micrographs and the corresponding selected area electron diffraction patterns of ST (b) and CRA (c) Ti-33Nb-4Sn specimens, and tensile stress-strain curves of ST and CRA Ti-33Nb-4Sn specimens (d).

Figure 2. Macrostress-lattice strain curves for $\{110\}\beta$, $\{200\}\beta$, $\{211\}\beta$, and $\{310\}\beta$ planes perpendicular to the loading direction.

Table. 1 Optimum SECs (GPa) that give the best fit to diffraction elastic constants (DECs) and anisotropy factor A (dimensionless) for CRA Ti-33Nb-4Sn alloy.

Table. 2 Experimental and calculated diffraction elastic constants (GPa) of CRA Ti-33Nb-4Sn alloy.

Figure 3. Shear moduli C' (a), shear modulus C_{44} (b), anisotropy factor A (c) and isotropic polycrystalline Young's moduli EH (d) of the CRA Ti-33Nb-4Sn alloy, along with those of β -type Ti-Cr, Ti-V and Ti-Nb single crystals as a function of e/a ratio.

Figure. 1

Figure. 2

Figure. 3

Table. 1 Optimum SECs (GPa) that give the best fit to diffraction elastic constants (DECs) and anisotropy factor A (dimensionless) for CRA Ti-33Nb-4Sn alloy.

	C_{11}	C_{12}	C_{44}	C'	A
Ti-33Nb-4Sn	126.8	101.6	22.4	12.6	1.78

Table. 2 Experimental and calculated diffraction elastic constants (GPa) of CRA
Ti-33Nb-4Sn alloy.

	$\{110\}^a$	$\{200\}$	$\{211\}$	$\{310\}$
Exp.	53.2±1.0	45.1±0.5	53.3±0.7	48.1±0.5
Cal.	53.4	45.7	53.3	47.9

^aAverage of the $\{110\}$ and $\{220\}$ crystal planes.