***In situ* synchrotron X-ray diffraction study of stress-induced martensitic
transformation in a metastable β -type Ti-33Nb-4Sn alloy**

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Abstract

In this study, the stress-induced martensitic (SIM) transformation of a recently developed metastable β -type Ti-33Nb-4Sn alloy consisting of a mixture of β and α'' phases are investigated by *in situ* synchrotron X-ray diffraction (SXRD). It is shown that though the SIM transformation covers a wide strain range, some remaining β phase is still observed after loading, indicating that the SIM transformation is incomplete. During SIM, the parameter of $b_{\alpha''}$ increases with macroscopic strain within the strain range of 1.5-4.7%, while the parameters of $a_{\alpha''}$ ($[100]_{\alpha''}$) and $c_{\alpha''}$ ($[002]_{\alpha''}$) remain constant or decrease with increasing strain, respectively. This provides a plausible explanation for why the $(020)_{\alpha''}$ peak intensifies, but the $(002)_{\alpha''}$ peak decreases and even eliminates in the loading direction during loading. Additionally, the activation sequence of different deformation mechanisms is clarified unambiguously.

Keywords: Titanium alloys; Tensile deformation behaviour; Phase transformation.

1. Introduction

Currently, metastable β -type titanium alloys are of great interests to the field of biomedical applications as Ni-free shape memory alloys due to their excellent biocompatibility, shape memory effect and superelasticity [1-3]. As is well known, the shape memory and superelastic properties in the metastable β -type Ti alloys are mainly based on a reversible martensitic transformation between austenitic β phase (bcc, space group Im3m) and martensitic α'' phase (C-orthorhombic, space group Cmcm) [4,5]. By adjusting the β -phase stability controlled mainly by the total content of β -stabilizers (e.g. Nb, Ta, etc.), the metastable β -type Ti alloys can exhibit a single α'' phase at room temperature and hence perform shape memory effect during the subsequent heating. With further improving the β -phase stability, a full β phase can be stabilized at room temperature and the alloys exhibit superelasticity originating from a stress-induced martensitic (SIM) transformation [5-7]. When the β -phase stability locates between the above two cases, a mixture of β and α'' phases can be obtained upon quenching from high temperature β -phase region. In such a case, neither excellent shape memory effect nor perfect superelasticity is found due to an incomplete martensitic transformation. Consequently, all previous investigations on the martensitic transformation behaviour were concentrated on single α'' or β -phase Ti alloys exhibiting shape memory effect or superelasticity [8-10].

Quite recently, it was reported that metastable β -type Ti alloys with a mixture of β and α'' phases also have a high potential for biomedical applications [11,12]. This is predominantly because that low elastic modulus, which is one of the most important properties for orthopedic implants, is obtained in metastable β -type Ti alloys with

compositions exhibiting a mixture of β and α'' phases upon quenching from β -phase region. Typically, Ti-33Nb-4Sn (wt. %) alloy, which displays a mixture of β and α'' phases upon quenching, can exhibit an ultralow Young's modulus of ~ 36 GPa after appropriate thermo-mechanical treatment [11]. It was also reported that the ultralow modulus of Ti-33Nb-4Sn (wt. %) alloy is closely related to its low β -phase stability with respect to α'' martensitic transformation [13]. However, the martensitic transformation behaviour in the Ti-33Nb-4Sn alloy has not yet been clarified in detail, although an in-depth understanding of this issue may provide help in establishing foundations for developing new Ti alloys, such as biomedical Ti alloy with ultralow elastic modulus.

X-ray diffraction has been used as a very powerful technique for studies of the martensitic transformation during tensile loading or heating. However, conventional X-ray sources cannot clearly distinguish the main peaks arising from β and α'' phases owing to their long wavelength and the coexistence of both $K_{\alpha 1}$ and $K_{\alpha 2}$ components [14]. In order to clearly distinguish the β and α'' peaks, *in situ* synchrotron X-ray source with a shorter wavelength and a better monochromaticity was employed in the present study.

In this study, an *in situ* synchrotron X-ray diffraction was carried out on a recently developed Ti-33Nb-4Sn (wt. %) alloy with a mixture of β and α'' phases, with the main interests being in the evolution of the martensitic transformation during uniaxial tensile loading and its influence on deformation behaviour.

2. Experimental procedure

A metastable β -type alloy with a nominal composition of Ti-33Nb-4Sn (wt. %) was used in the present study. Upon melting, homogenizing, forging and quenching

from high temperature β -phase region, the alloy was then cold rolled to a plate at a thickness reduction of $\sim 87\%$. A more detailed description of fabricating Ti-33Nb-4Sn alloy can be seen in our previous reference [12]. In the present paper, the cold rolled plate was solution treated at 1073 K for 1 hour, followed by quenching into water (~ 298 K). The corresponding specimens will be abbreviated as ST specimens henceforth.

Conventional X-ray diffraction (XRD) characterization was conducted on a Rigaku D/max 2550 diffractometer with Cu K α source. Macroscopic uniaxial tensile test was carried out along the rolling direction, using an Instron-8801 testing system. *In situ* synchrotron X-ray diffraction (SXRD) was conducted on beam line 11-ID-C at the Advanced Photon Source (APS) at Argonne National Laboratory. High-energy X-rays with a beam size of 0.6 mm $\times$ 0.6 mm and wavelength of 0.10798 Å were used to obtain Debye-Scherrer diffraction rings during loading. The Debye-Scherrer rings were calibrated in Fit2D software and output one-dimensional (1-D) patterns for analysis.

3. Results and discussion

Fig. 1 shows the initial SXRD pattern of ST Ti-33Nb-4Sn alloy before loading. The diffraction peaks from both β and α'' phases are observed from Fig. 1 and its inset (a), indicating that the ST Ti-33Nb-4Sn alloy consists of a mixture of β and α'' phases. By comparing Fig. 1 and its inset (b), one can see that the diffraction peak from (002) $_{\alpha''}$ (marked by the black diamond) is clearly visible alongside $\{110\}_{\beta}$ by SXRD technique (Fig. 1), while this (002) $_{\alpha''}$ peak cannot be separated by conventional XRD (inset b). This suggests that compared with conventional XRD, SXRD has higher resolution and thus can provide more precise detail in phase transformation. It can also be seen from Fig. 1 that the diffraction intensity of $\{110\}_{\beta}$ is much higher than that of $\{211\}_{\beta}$. This

can be attributed to the fact that a strong $\{hkl\}\langle 110 \rangle_{\beta}$ texture is often formed in β -type Ti alloys subjected to solution treatment following cold rolling [15,16].

Fig. 2(a) displays part of the straightened Debye-Scherrer diffraction rings of ST Ti-33Nb-4Sn alloy during loading at different strain levels. Overall, the intensity of α'' spots increases as the applied strain increases during loading, together with a decrease in the intensity of β spots, indicating that a progressive SIM transformation occurs during loading. This SIM transformation makes the texture of β and α'' phases increasingly obvious, as evidenced by the observation that the intensity distribution of β and α'' spots along the straightened diffraction rings becomes more and more uneven during loading. The highly developed texture allows a precise determination of the orientation relationship between the parent β phase and α'' martensite. The original Debye-Scherrer diffraction rings of ST Ti-33Nb-4Sn alloy at a strain of 14% are given in Fig. 2(b). The lattice correspondence between the β and α'' phases can be seen directly as follows: $(100)_{\beta} \parallel (100)_{\alpha''}$, $(011)_{\beta} \parallel (010)_{\alpha''}$ and $(0\bar{1}1)_{\beta} \parallel (001)_{\alpha''}$. Furthermore, some angles between the β and α'' crystallographic planes can also be measured straightforwardly, e.g., $54.6 \pm 1^{\circ}$ for the angle between the $(011)_{\beta}$ and $(110)_{\alpha''}$ planes and $32.2 \pm 1^{\circ}$ for the angle between the $(011)_{\beta}$ and $(131)_{\alpha''}$ planes, respectively. The present results are in good agreement with the crystallographic orientation relationship obtained by the phenomenological theory of martensitic transformation in a previous study [17], where the angle between the $(011)_{\beta}$ and $(110)_{\alpha''}$ planes is $\sim 53.9^{\circ}$ and the angle between the $(011)_{\beta}$ and $(131)_{\alpha''}$ planes is $\sim 34.3^{\circ}$. This slight difference in crystallographic orientation relationship between the present results and the previous computational results might be attributed to different alloy systems, i.e., Ti-33Nb-4Sn alloy for the present study and Ti-36.9Nb-2.0Ta-3.0Zr-0.30O alloy for the previous

computation.

Fig. 3(a) shows the spectral evolution with macroscopic strain in the loading direction (i.e., a 10° azimuthal bin around 90° and 270°) within the d -spacing range of 2.2-2.6Å. Overall, the d -spacing of $\{110\}_\beta$ (marked by the blue circle) increases monotonically with increasing macroscopic strain up to 4.7%, where the $\{110\}_\beta$ peak vanishes. In contrast, the $(002)_{\alpha''}$ peak (labeled by the black diamond) decreases with increasing macroscopic strain and finally disappears at a strain of 2.1%. In the case of $(020)_{\alpha''}$ (marked by the red square), the d -spacing increases with increasing macroscopic strain to 4.7% and then stays about constant with further increasing macroscopic strain.

Here, an important point to note is that the intensity of diffraction peaks in Fig. 3(a) only stands for the volume fractions of individual diffraction peaks along the loading direction, which is inadequate to reveal the evolution of martensitic transformation between the β and α'' phases as a whole. Typically, although the $\{110\}_\beta$ peak disappears at a strain of 4.7% in the loading direction, the spots from $\{110\}_\beta$ can be clearly visible even at a high strain of 14% in the Poisson's direction (Fig. 2b). Thus, in the present study, the evolution of the volume fractions of the $\{110\}_\beta$, $(002)_{\alpha''}$ and $(020)_{\alpha''}$ peaks was characterized by the integrated intensity of the whole Debye-Scherrer diffraction rings (i.e., $0^\circ \leq$ azimuthal angles $\leq 360^\circ$). The relative integrated intensity for the $\{110\}_\beta$, $(002)_{\alpha''}$ and $(020)_{\alpha''}$ peaks as a function of macroscopic strain is plotted in Fig. 3(b), where all the values for the $\{110\}_\beta$, $(002)_{\alpha''}$ and $(020)_{\alpha''}$ peaks are normalized by their respective intensity values at a strain of 0%. It can be seen that the relative integrated intensity of $\{110\}_\beta$ begins to decrease at a strain of about 0.5% and continuously decreases sharply at a high rate to a strain of $\sim 4.7\%$, and then decreases

gradually at a low rate up to a strain of $\sim 14\%$. At the same time, the relative integrated intensity of $(002)_{\alpha''}$ and $(020)_{\alpha''}$ increases firstly at a high rate and then increases at a low rate. This suggests that the SIM transformation starts at a strain of $\sim 0.5\%$, and occurs rapidly within the strain range of $0.5\text{--}4.7\%$ but slowly within the strain range of $4.7\text{--}14\%$. Bearing in mind that a relative integrated intensity of 0.79 can still be observed for $\{110\}_{\beta}$ at 14% of strain in Fig. 3(b), therefore, the SIM transformation in ST Ti-33Nb-4Sn alloy is incomplete, with some residual β not being transformed. Besides, it should be noted that in addition to the SIM transformation, the reorientation of pre-existing martensite variants formed before loading (i.e., quenching) also occurs during loading, as proven by the fact that the $(002)_{\alpha''}$ peak starts to decrease from $\sim 0.5\%$ strain and even vanishes at $\sim 2.1\%$ of strain in the loading direction (Fig. 3a), although the whole integrated intensity of $(002)_{\alpha''}$ begins to increase from $\sim 0.5\%$ strain (Fig. 3b). The combined effects of SIM transformation and martensite variants reorientation lead to intensifying $(020)_{\alpha''}$, but decreasing and even eliminating $(002)_{\alpha''}$ and $\{110\}_{\beta}$ peaks in the loading direction (this will be discussed later).

Fig. 4(a) shows the evolution of lattice parameter (a_{β}) of β parent phase with macroscopic strain during loading. It is clear that the a_{β} increases with increasing strain to 4.7% and then remains almost constant with further increasing strain. Obviously, the increase of a_{β} to 4.7% strain corresponds to the elastic deformation of β phase, while the constant of a_{β} , irrespective of further increasing strain, is attributed to the plastic deformation of residual β . The evolution of the lattice parameters ($a_{\alpha''}$, $b_{\alpha''}$ and $c_{\alpha''}$) of α'' phase during loading is given in Fig. 4(b). The parameter of $a_{\alpha''}$ remains roughly constant during the whole loading, while the $c_{\alpha''}$ parameter keeps approximately constant firstly, then decreases slightly within the strain range from 1.5% to 4.7% , and

finally remains roughly constant with further increasing the strain. Compared with the evolution of $a_{\alpha''}$ and $c_{\alpha''}$, the evolution of $b_{\alpha''}$ is more valuable, though seemingly more complicated. In the case of $b_{\alpha''}$, the parameter increases slightly with increasing strain to 0.5% due to the elastic deformation of pre-existing α'' martensite that was formed during quenching before loading. Within the strain range from 0.5% to 1.5%, the parameter of $b_{\alpha''}$ remains roughly constant, accompanied by the co-occurrence of the reorientation of pre-existing martensitic variants and SIM transformation (Fig. 3). With further increasing strain to 4.7%, the parameter of $b_{\alpha''}$ increases monotonically with increasing strain, which corresponds to the elastic deformation of the re-oriented and stress-induced α'' martensite. When the strain exceeds 4.7%, the $b_{\alpha''}$ keeps roughly constant with increasing the strain, corresponding to the plastic deformation of α'' martensite.

The evolution of the lattice parameters of β and α'' phases can provide a plausible explanation for why the combined effects of SIM transformation and the reorientation of martensite variants can lead to intensifying $(020)_{\alpha''}$ peak, but decreasing and even eliminating $(002)_{\alpha''}$ and $\{110\}_{\beta}$ peaks in the loading direction (Fig. 3). According to the crystallographic orientation relationship between β and α'' phases, some of $\langle 100 \rangle_{\beta}$ will transform to $[100]_{\alpha''}$ (i.e., $a_{\alpha''}$ -axis) while some of $\langle 110 \rangle_{\beta}$ will transform to either $[020]_{\alpha''}$ (i.e., $b_{\alpha''}$ -axis) or $[002]_{\alpha''}$ (i.e., $c_{\alpha''}$ -axis), which gives rise to 6 equivalent lattice correspondences between these two phases and the corresponding 12 habit plane martensite variants [18,19]. During quenching from high temperature β -phase field, many different types of martensite variants can be formed in a self-accommodation manner [20], as evidenced by the presence of multiple diffraction peaks of α'' martensite along a specific direction, e.g., the coexistence of $(020)_{\alpha''}$ and $(002)_{\alpha''}$ along

the loading direction (Fig. 3a). However, if the pre-existing α'' martensite is exposed to the external stress or a SIM transformation is activated by the external stress, the reorientation of pre-existing martensite variants or the selection of the newborn martensite variants will be operated, resulting in that only the variants that give a maximum of strain, i.e., accommodate the external strain to the greatest extent, can survive or form during loading [8,21]. As shown in Fig. 4(b), the parameter of $b_{\alpha''}$ increases monotonically with increasing strain within the strain range from 1.5% to 4.7%, while the parameters of $a_{\alpha''}$ and $c_{\alpha''}$ remain constant or decrease with increasing strain, respectively. Meanwhile, the macroscopic strain expands during loading in the loading direction. In such a case, the variants that give a maximum of expansile strain in the loading direction, i.e., accommodate the macroscopically expansile strain to the greatest extent, can survive or form during loading [8,21]. Therefore, it is believed that in the present ST Ti-33Nb-4Sn alloy, the α'' variants, with the $b_{\alpha''}$ -axis ($[020]_{\alpha''}$) being parallel to loading direction and the $a_{\alpha''}$ - and $c_{\alpha''}$ - axis ($[100]_{\alpha''}$ and $[002]_{\alpha''}$, respectively) being normal to loading direction, will be formed preferentially to accommodate the external strain during loading. As a result, the $(020)_{\alpha''}$ peak intensifies but the $(002)_{\alpha''}$ peak decreases and even vanishes with increasing strain in the loading direction due to the combined effects of SIM transformation and the reorientation of martensite variants.

The tendency in the evolution of the lattice parameters of β and α'' phases (within the strain range of 1.5-4.7% in Fig. 4a~b) is similar with that in a fully β -phase Ti-24Nb-0.5O alloy where the parameter of $b_{\alpha''}$ increases and the parameter of $c_{\alpha''}$ decreases during the variant selection of stress-induced martensitic transformation [22]. A possible reason for this similarity is that there is no significant difference in the

crystallographic orientation relationship between β and α'' phases for the ($\beta+\alpha''$)-phase Ti-33Nb-4Sn alloy and β -phase Ti-24Nb-0.5O alloy.

On the basis of the above results shown in Fig. 3 and Fig. 4a~b, the activation sequence of different deformation mechanisms of ST Ti-33Nb-4Sn alloy can be clarified unambiguously (see Fig. 4c). At the initial deformation stage, the pre-existing α'' and β phases concurrently experience elastic deformation to 0.5% strain. Next, the reorientation of pre-existing α'' variants occurs in the 0.5-2.1% strain range, where the SIM transformation concurrently takes place. Within the strain range of 1.5-4.7%, the re-oriented and SIM α'' variants are deformed elastically, together with the elastic deformation of residual β phase and the progressive occurrence of SIM transformation. For higher strain in excess of 4.7%, the re-oriented and SIM α'' martensite and the residual β phase were mainly deformed plastically. In this stage, the SIM transformation from β to α'' still occurs, though at a relatively low rate. This is attributed to the fact that in this stage, the macroscopic stress does not significantly increase with increasing macroscopic strain any more, due to the occurrence of plastic deformation.

4. Conclusion

In summary, an *in situ* synchrotron X-ray diffraction was conducted on a recently developed metastable β -type Ti-33Nb-4Sn alloy consisting of a mixture of β and α'' phases to investigate its SIM transformation. During the uniaxial tensile loading, the SIM transformation between austenitic β and martensitic α'' phases takes place in a wide strain range of 0.5-14%. Nevertheless, this SIM transformation is incomplete, with some residual β not being transformed at a strain of 14%. The SIM transformation intensifies the texture of β and α'' phases, allowing a precise and direct determination

of the orientation relationship between the parent β phase and α'' martensite. During the SIM transformation, the parameter of $b_{\alpha''}$ ($[020]_{\alpha''}$) increases monotonically with macroscopic strain within the strain range of 1.5-4.7%, whereas the parameters of $a_{\alpha''}$ ($[100]_{\alpha''}$) and $c_{\alpha''}$ ($[002]_{\alpha''}$) stay about constant or decrease with macroscopic strain, respectively. This provides a plausible explanation for why the combined effects of SIM transformation and the reorientation of martensite variants can lead to intensifying $(020)_{\alpha''}$ peak, but decreasing and even eliminating $(002)_{\alpha''}$ and $\{110\}_{\beta}$ peaks in the loading direction. On the basis of the results of *in situ* synchrotron X-ray diffraction, the relationship between macroscopic stress-strain curve and different deformation mechanisms, involving elastic and plastic deformation of β phase, elastic deformation of the pre-existing α'' , re-oriented and SIM α'' variants, reorientation of the pre-existing α'' , SIM transformation, plastic deformation of the re-oriented and SIM α'' martensite, is clarified unambiguously.

Acknowledgments

The authors greatly appreciate the financial support from the National Natural Science Foundation of China (51401088, 51601217, 51471017, 51601069), the Special Financial Grant from the China Postdoctoral Science Foundation (2016T90424), the Natural Science Foundation of Jiangsu Province (BK20140549, BK20160514, BK20160255) and the Opening Project of Jiangsu Key Laboratory of Advanced Structural Materials and Application Technology (ASMA201502). The use of the Advanced Photon Source was supported by the US Department of Energy, Office of Science, and Office of Basic Energy Science, under Contract No. DE-AC02-06CH11357.

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Figure captions:

Figure 1. Initial SXRD pattern of ST Ti-33Nb-4Sn alloy before loading (i.e., at a macroscopic strain of 0%). Inset (a) is an enlarged SXRD pattern within the d -spacing range of 1.25-1.45 Å, showing clearly the presence of α'' martensite. Inset (b) is the convention XRD profile of ST Ti-33Nb-4Sn alloy before loading. Notice the presence (Fig. 1) and absence (inset b) of (002) $_{\alpha''}$ diffraction peak characterized by the SXRD and convention XRD techniques, respectively.

Figure 2. Part of the straightened Debye-Scherrer diffraction rings of ST Ti-33Nb-4Sn alloy during loading at different strain levels (a). Original Debye-Scherrer diffraction rings of ST Ti-33Nb-4Sn alloy at a strain of 14% (b), where the lattice correspondence between the β and α'' phases can be observed directly.

Figure 3. Spectral evolution (within the d -spacing range of 2.2-2.6 Å) with macroscopic strain in the loading direction (i.e., a 10° azimuthal bin around 90° and 270°, Fig.3a).

Relative integrated intensity for the $\{110\}_\beta$, $(002)_{\alpha''}$ and $(020)_{\alpha''}$ peaks as a function of macroscopic strain (b). Notice the existence of residual β even at a strain of 14% (b), showing this SIM transformation from austenitic β phase to martensitic α'' phase is incomplete.

Figure 4. Evolution of lattice parameters of β (a) and α'' (b) phases with macroscopic strain during loading. Regions of occurrence of different deformation mechanisms are represented on macroscopic stress-strain curve of Ti-33Nb-4Sn (c).