**High-energy X-ray diffuse scattering studies on
deformation-induced spatially-confined martensitic transformations
in multifunctional Ti-24Nb-4Zr-8Sn alloy**

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Abstract

Two main arguments exist concerning the deformation mechanisms in Ti-Nb based gum metals, i.e. formation of reversible nanodisturbance and reversible stress-induced martensitic transformation. In this work, we used the in-situ synchrotron-based high-energy X-ray diffuse-scattering technique to reveal the existence of a specific deformation mechanism, i.e., deformation-induced spatially-confined martensitic transformations, in Ti-24Nb-4Zr-8Sn-0.10O single crystals with cubic β parent phase, which explains well some anomalous mechanical properties of the alloy such as low elastic modulus and nonlinear superelasticity. Two kinds of nano-sized martensites with different crystal structures were found during uniaxial tensile loading along $[110]_{\beta}$ axis at room temperature and 190 K, respectively. The detailed changes in the martensitic phase transformation characteristics and the transformation kinetics were experimentally observed at different temperatures. The domain switch from non-modulated martensite to modulated one occurred at 190 K, with its physical origin attributed to the heterogeneity of local phonon softening depending on temperature and inhomogeneous composition in the parent phase. The in-depth understanding of the formation of stress-induced spatially confined nano-sized martensites with a large gradient in chemical composition may benefit designs of high-strength and high-ductility alloys.

Keywords: Titanium alloys; Martensitic transformation; Nanodomains; Synchrotron diffraction; Nonlinear superelastic behavior

1. Introduction

Titanium alloys have been used widely in structural, chemical and biomedical applications [1, 2]. The development of multifunctional Ti alloys with high strength, low elastic modulus, superelasticity with narrow hysteresis and excellent ductility has recently attracted great attentions. In order to obtain a low elastic modulus and outstanding mechanical properties, metastable β -type titanium alloys have been developed by adding different alloying elements. For example, Saito et al. [3] found a new multifunctional alloy with a body-centered cubic (bcc) structure by the addition of elements from the group Va (Ta, Nb, V) and IVa (Zr, Hf), and a certain amount of oxygen. This alloy, called gum metal (GM), was designed in the chemical composition to acquire a valence electron number (e/a) of 4.24. Based on the density function theory, the nearly equal elastic constants C_{11} and C_{12} lead to extremely low elastic shear modulus at e/a ratio of 4.24 [4, 5]. The low ideal strength of metallic solid induced by the elastic instability (low elastic shear modulus) results in the dislocation-free plasticity mechanism that accommodates plastic strain through the growth of nanodisturbances [6] to produce giant faults [7, 8]. The formation of nanodisturbances instead of conventional dislocations could elucidate its anomalous mechanical properties, such as high strength, nonlinear elastic behavior and excellent ductility [9-12]. Recently, another new family of titanium alloy system Ti2448 (abbreviated from chemical composition of Ti-24Nb-4Zr-8Sn-0.10O in weight percent) has been developed with an e/a ratio of ~ 4.15 , which is close to the value of 4.24 for GMs. The Ti2448 alloy possesses a Young's modulus below 50 GPa with 3.3% recoverable strain,

low Poisson's ratio of 0.14 and an ultrahigh strength of ~0.9 GPa [13]. It was proposed that the easy crystal distortion due to much weakened chemical bonding of atoms is responsible for achieving high strength and large-scale elastic deformation in this alloy system [14].

However, besides the deformation mechanisms intrinsically induced by elastic instability, other deformation mechanisms were also reported in the GMs and Ti2448 alloy, such as dislocation slide [15, 16], deformation twinning [16-18] and stress-induced martensitic transformation [18-20]. It is generally considered that the peculiar elastic behavior in metastable β -type titanium alloys could be attributed to the stress-induced martensitic transformation from β (bcc) to an orthorhombic α'' phase [18-22]. The stress-induced martensitic transformation occurred in GMs was in obvious contrast to the conventional martensitic transformation with self-accommodating ploytwinned structures, but confined to be nanodomain-like morphology [20, 22]. The formation of confined nanodomains of martensite variants was also clearly observed in GMs with new physical phenomenon related to Invar effect during cooling [21, 23]. Meanwhile, the stress-induced martensite with nanodomain-like morphology has also been evidenced during tensile loading in Ti2448 alloys [14, 24, 25], which is similar to that found in GMs. It could thus be inferred from the above-mentioned findings that the formation of nano-sized martensites is a common phenomenon in the gum-like metastable β -type titanium alloys.

It has been well known that the martensite with strain glass state, being a kind of typical spatially-confined martensite, was extensively found in the ferroelastic

Ti-Ni-based alloy systems [26-28]. Unlike a typical martensite with long-range strain ordered state, the growth of martensite in the strain-glassy Ti-Ni alloys was confined due to the inhomogeneous long-range stress field caused by doping a large amount of point defects. However, it is still unclear whether the mechanism of impurity doping could explain the formation of confined martensite in the single crystal of Ti₂Al and GMs. Moreover, the spatially-confined martensite in various alloy systems was always found with decreasing temperature [21, 23]. But few attempts to date in the literature were made for clarifying the relationship between the stress-induced confined martensitic transformation and anomalous mechanical behaviors.

It is suggested that the contradictory nature of deformation mechanisms, i.e. dislocation-free mechanism [3] and reversible stress-induced martensitic transformation, exhibited in gum-like metastable β -type titanium alloys could be influenced by the small changes in composition and materials processing [12, 21]. The alloys studied by Talling et al. [20] were prepared by melting and casting, which could introduce local elemental segregation and trigger the process of martensitic transformation. But the specimens prepared by powder metallurgy would exhibit more homogeneous chemical composition and could be deformed via the dislocation-free mechanism [12]. Here we used the approach of melting and forging to prepare samples, and then fabricated the single crystal with optical floating-zone furnace, for revealing the effect of the local inhomogeneous chemical composition on the confined martensitic transformation.

The present work will focus on the investigation of the detailed martensitic

transformation behavior in Ti2448 alloy at room temperature (RT) and 190 K by in-situ synchrotron-based high-energy X-ray diffuse-scattering (HE-XRDS) experiments, which could reveal its specific deformation mechanism giving rise to the anomalous mechanical behaviors, such as the low elastic modulus and nonlinear superelastic behavior. In addition, we aim to clarify the intrinsic origin on the formation of nano-sized martensite related to inhomogeneous chemical composition by the transmission electron microscopic observation. The in-depth understanding of the detailed process of martensitic transformation could shed light on the development of new multifunctional titanium alloys with excellent mechanical properties for applications through the strategy of nanostrain-domain martensitic transformation.

2. Materials and experimental methods

2.1 As-received material and sample preparation

Ingots with compositions of Ti-24Nb-4Zr-8Sn-0.1O (abbreviated as Ti2448) in mass% were prepared by arc melting and hot forged at 1273 and 1123 K into bars 25 mm in diameter. Single crystals were grown from ingots by an optical floating-zone furnace (FZ-T-12000-X-VP-S, Crystal System Inc.) at a crystal growth rate of 5 mm·h⁻¹ under high-purity flowing argon protection. The detailed technique for obtaining single crystal was well described previously [14]. The tensile specimens were cut from single crystal ingots along the crystallographic <110> direction of β phase and the direction was parallel to the tensile direction within an accuracy of 1° which was determined by Laue X-ray back reflection technique. Chemical and gas analyses showed that oxygen

contents took up ~0.1 wt.%. The cross-section dimensions of the tensile specimens were approximately 2.9×0.8 mm.

2.2 Experimental methods

In-situ synchrotron-based HE-XRDS experiments were conducted on the beamline 11-ID-C of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). A monochromator with a Si(113) single crystal was used to produce an X-ray beam with an energy of 115 keV (wavelength 0.10801 Å) and a loading frame controlled by displacement was in-situ applied to the dog-bone-shaped sample for studying the change of the scattering patterns to trace the evolution of crystallographic structure and lattice strain under the tensile loading. The loaded specimen could be rocked within $\pm 5^\circ$ along the loading or transverse rotation axis simultaneously in order to obtain abundant information of reciprocal space. Diffraction patterns were recorded by a two-dimensional (2D) detector (Perkin Elmer amorphous silicon) installed in the front of loaded sample.

Transmission electron microscopy (TEM), high resolution (HR)-TEM, high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) and energy-dispersive X-ray (EDX) analyses were conducted on a JEOL ARM 200F microscope (JEOL, Tokyo, Japan) operated at 200 kV to examine the initial microstructure of specimens.

3. Results

3.1. Confined martensitic transformation behavior at RT

Uniaxial tensile loads were applied along the $\langle 110 \rangle$ direction of the Ti2448 single crystal, and the in-situ HE-XRDS measurements were performed along $[001]_{\beta}$ zone axis at RT. Fig. 1a shows the primary diffraction spots of the initial bcc structure of Ti2448 prior to loading, in combination with some weak diffuse scattering signals as indicated by solid circles. It is noted that the nearly equal intensity of these weak diffuse scattering signals reveals that at least two kinds of variants of α'' martensitic domains exist in the initial parent matrix [29].

With increasing tensile stress, the variant selection occurs for α'' martensitic domains and results in the formation of oriented variants of α'' martensitic domains, as evidenced by the vanishing of equivalent $(021)_{\alpha''}$ diffuse scattering signals in the solid circles of Fig. 1b. Finally, the weak diffuse scattering signals become diffraction spots, indicating the formation of oriented nano-sized α'' martensite from the growth of oriented α'' martensitic particles under uniaxial tension.

Based on the orientation relationship between α'' and β phases, i.e. $(110)_{\beta} // (010)_{\alpha''}$ and $[001]_{\beta} // [100]_{\alpha''}$ [20], the $(220)_{\beta}$ diffraction spot would split into two distinguishable spots corresponding to α'' and β phases, respectively, under certain loading. The in-situ observation of such split spot could provide detailed information on the phase transformation procedure even for nano-scaled domains with a small volume fraction [30]. Figs. 1c-1f highlight the detailed change of $(220)_{\beta}$ diffraction spot indicated by solid square in Fig. 1a at different applied stresses noted in figures. An obvious change from the single peak into double peaks can be found as indicated by the Bragg peak

shift (to low angle with a large d-spacing, as noted from peak position marked by solid line to that by dotted dash line) and finishing separation, indicating a phase transformation from β to α'' . Surprisingly, besides the diffraction peak splitting due to the appearance of new spot $(040)_{\alpha''}$ (indicated by dotted dash line), the d-spacing of $(220)_{\beta}$ spot also has a sudden increase as shown in peak shift toward low angle at the stress stage of 176 MPa, shown by the dash line, which verifies that there is another phase transformation from β to a new phase. Our subsequent HE-XRDS experiments verify the new phase, named as δ phase, with an orthorhombic structure. The difference between two martensites, i.e. α'' and δ , will be discussed beneath.

The evolution of 1-dimensional (1D) diffraction profiles for $(021)_{\alpha''}$ noted in Fig. 1b as a function of stress is shown in Fig. 2a. The change in the diffuse scattering integral intensity of $(021)_{\alpha''}$ peak could stand for the volume fraction (VF) variation of the oriented α'' martensitic variants along loading direction (inset of Fig. 2a). It could be seen that the VF of the oriented α'' phase increases slowly between O-A stress section corresponding to the domain switch from other variant of α'' martensite. The looped curve for the change of VF suggests that the β - α'' phase transformation is reversible.

The 1D HE-XRDS diffraction profiles stemmed from $(220)_{\beta}$ spot show a large shift toward the lower Bragg angle owing to phase transformation (Fig. 2b). The visible peak asymmetry at the stress of 490 MPa (inset of Fig. 2b) reveals the existence of two overlapped peaks from α'' and δ . The Lorentz function was employed to separate these two overlapped peaks under the assumption that the full width at half maximum (FWHM) of $(021)_{\alpha''}$ could be used as a criterion to fit the $(040)_{\alpha''}$ in the overlapped

$(220)_\beta$ peak. It is obvious to find that the FWHM is narrow for α'' martensite but broad for δ martensite. Derived from FWHM of corresponded phase, the evolution of domain size (Dv) for each phase could be calculated based on the Debye-Scherrer formula, $Dv = \lambda / (H \cdot \cos\theta)$ (where λ is the wavelength of the radiation and H is the integral breadth of a reflection located at 2θ) [31]. The Dv of α'' phase increases to 8 nm and then remains almost constant under further increased applied stress. However, the Dv of δ phase remains at a rather small scale ~ 3.4 nm due to its much broader FWHM. The nano-sized α'' and δ martensites maintain co-existence even at the maximum stress as evidenced by the inset of Fig. 2b.

The martensitic phase transformation can be clearly understood from the evolution of elastic lattice strain of the crystalline planes by tracing the change in lattice spacing for different (hkl) planes with respect to the initial interplanar spacing, i.e. $\varepsilon_{hkl} = (d_{hkl} - d_0) / d_0$, where d_{hkl} and d_0 correspond to the interplanar spacing (d-spacing) of specific hkl planes with and without an external stress, respectively. For austenitic phase, d_0 is determined from the value of d-spacing of stress-free sample, while for the martensite, d_0 is counted as the initial d-spacing of the diffraction plane of austenite having a fixed crystal orientation relationship with the martensite. Fig. 2c shows the change of lattice strain for β 、 α'' and δ phases as a function of applied stress. The large jump in lattice strain (noted as A-B) verifies the existence of phase transformation from β to δ more directly. Based on the same method, the transverse $(2\bar{2}0)_\beta$ peak could be separated as $(004)_{\alpha''}$ and $(004)_\delta$ peaks, respectively. The martensitic transformation induces an increase of transverse lattice strain plotted in Fig. 2d rather than a reduction

according to the traditional Poirier's ratio theory. After the stress stage B, the parent β phase could be considered having a complete martensitic transformation. Thus two lattice parameters of α'' and δ phases, i.e. b and c for orthorhombic structure, could be obtained according to the orientation relationship, i.e. $(110)_\beta // (020)_{\alpha''} // (020)_\delta$ and $[\bar{1}\bar{1}0]_\beta // [002]_{\alpha''} // [002]_\delta$ (Table 1).

3.2. Phase transformation scenario at RT

In order to further understand the detailed martensitic transformation procedure and the difference between α'' and δ martensites, the in-situ HE-XRDS observation from different incident beam direction is necessary. Fig. 3a shows the standard diffraction spots of the Ti2448 single crystal along $[110]_\beta$ beam direction before loading. The weak diffuse scattering signals of α'' phase could also be seen as shown by solid circles. While the applied stress reached 202 MPa, two kinds of stress-induced martensites, i.e. α'' and δ , replaced the parent phase (Fig. 3b). Due to the absence of diffraction spot at $1/3$ and $2/3$ position of $\{112\}_\beta$, the new phase could not be indexed as ω phase by the direct evidence in Fig.3b. Meanwhile, the d -spacing of $(110)_{\alpha''}$ and $(110)_\beta$ can be calculated as 2.3307 and 2.3818 Å at 202 MPa, respectively. It could not thus be concluded that these two diffraction spots belong to equivalent crystal plane of $\{1\bar{1}00\}_\alpha$ due to large lattice strain ($\sim 2.196\%$) between them [32]. Analogous to the in-situ HE-XRDS study of Figs. 1c-1f, Figs. 3c-3f observe the evolution of $(220)_\beta$ spot in three dimensional (3D) reciprocal space with increasing tensile stress. At the stress stage of 135 MPa (Fig. 3d), two separated diffraction spots of α'' appeared at nearly $\pm$

45° direction below the β spot. However, the appearance of diffraction spots for δ was delayed in comparison with the formation of α'' martensite as evidenced by Fig. 3e. It indicates the formation of δ martensite needs to overcome larger energy barrier than α'' martensite. Then, with continuously increasing loading, two separated α'' diffraction spots integrated into one large diffraction spot, which is different from two remained diffraction spots (separated with $\sim 2.6^\circ$) for δ in Fig. 3f. The diffraction spots for both α'' and δ indeed co-exist at the maximum stress, which is similar to that observed in Fig. 1f.

Fig. 4a shows the evolution of transverse lattice strain of $(002)_\beta$ as a function of tensile stress. The region A-B indicates the stress-induced martensitic transformation from β to δ and the lattice strain at the point B could be used for determining another lattice parameter for α'' and δ based on the orientation relationship, i.e. $(002)_\beta/(200)_{\alpha''}/(200)_\delta$ (Table 1). The change in the cell volume obtained by the multiplication operation of three unit cell directions (displayed in the inset of Fig. 4b), shows a slight decrease ($\sim -0.9\%$) from β to δ phase transformation. However, the phase transformation from β to α'' causes an expansion of cell volume ($\sim 0.36\%$). The difference in cell volume between the two kinds of martensites increases the ability of strain accommodation due to the compensated lattice mismatch between them if they could transform each other.

3.3. Phase transformation scenario at 190 K

The in-situ HE-XRDS observation of the dual martensitic phase transformation

scenario was conducted at 190 K along $[1\bar{1}0]_{\beta}$ beam direction for the Ti2448 single crystal with the applied load along $\langle 110 \rangle_{\beta}$ direction. Fig. 5a and Fig. 5b present the 2D diffraction patterns before and under loading, respectively. The $(220)_{\beta}$ diffraction spot (noted as solid square) is still chosen as the target for in-situ observation. The diffraction spots of α'' already appeared prior to loading for the specimen cooled at 190 K as shown in Fig. 5c, which indicates that the nano-sized α'' martensite was formed under cooling. The size of α'' martensite can be estimated as ~ 10 nm based on the FWHM of $(110)_{\alpha''}$ diffraction spots.

Upon a small loading (13 MPa) was applied, two diffraction spots with broad peak for δ martensite appeared as indicated in Fig. 5d, suggesting the formation of the nano-sized δ martensite. The formation of δ martensite was delayed in comparison with the appearance of α'' martensite at 190 K as well, which indicates that the transformation energy barrier for α'' is indeed lower than that for δ . However, in contrast with the RT deformation, the diffraction spot of δ phase became weak with further increasing applied stress and finally merged together into one diffraction spot for α'' at 47 MPa. The final size of α'' martensite grew to 11.9 nm at 47 MPa (as shown in Fig. 5f). It can thus be inferred from the above finding that δ martensite could be switched into α'' martensite under the external stress at 190 K.

The evolution of 1D diffraction profile of $(220)_{\beta}$ is shown in the inset of Fig. 6. It can be seen that the peak profile of $(040)_{\alpha''}$ is symmetric after the stress stage of A, which indicates the lattice mismatch between α'' and δ phases is almost disappear, i.e. the δ phase transformed to α'' phase finally. The nearly linear relationship (displayed in

the A-B stage in Fig. 6) in the $(040)_{\alpha''}$ lattice strain vs. stress curve also proves that only α'' phase exists after the applied stress excessing A due to lacking in interaction between α'' and δ phases. To understand the difference in the martensitic transformation characteristics at RT and 190 K, it is necessary to explore the origin of the formation of two different martensites by HR-TEM.

3.4. TEM Investigation

The TEM observation was conducted to the initial microstructure of Ti2448 single crystal at RT. Fig. 7a is the HAADF-STEM image with the electron beam along the $[100]_{\beta}$ direction. The bright spots stand for atoms and the intensity of spots is proportional to the atomic number in a HAADF image. By adjusting of the image contrast, the bright spots (the heavy Z atoms) are observed easily in the Fig. 7a. It can be seen that the nanodomains with heavy atoms (noted as dashed circles) or light atoms (noted as solid circles) are both distributed randomly.

The existence of two kinds of heavy-atoms (Nb, Zr, or Sn)-rich and light-atoms (Ti)-rich phase-separated clusters indicates the heterogeneous nature of the austenite. The scale of the compositional non-uniformity in austenite matches the scale of the martensitic nanodomains. The Nb-rich areas could be considered as the B2-ordered structure that is different from Ti-rich areas with the bcc-disordered structure. The selected area electron diffraction pattern for Ti2448 alloy along the $[110]_{\beta}$ direction shows the diffuse scattering signal $(110)_{\alpha''}$ in the inset of Fig. 7b (noted as solid circle), while its corresponding dark field image reveals the random distribution of α''

nano-nuclei and B2 clusters inside the disordered bcc matrix (Fig. 7b).

According to the above TEM observation and HE-XRDS characterization, the confined dual martensitic transformation mechanism during deformation of gum-like Ti2448 alloy could be established. The initial microstructure of Ti2448 single crystal is non-uniform in both structure and composition and consists of three parts, i.e. Nb-rich B2 regions, Nb-rich α'' martensitic particle regions and Nb-lean bcc regions. With increasing applied stress, the α'' martensites were generated via either growth of α'' martensitic embryos or the direct phase transformation from Nb-rich B2 regions, while the Nb-lean bcc regions are easily transformed to δ martensite. Therefore, due to different atomic occupation of heavy atoms (Nb, Sn, Zr) in α'' and δ phases, the crystallographic structure of α'' and δ are finally determined as the C222 ordered orthorhombic structure (space group No.21) and the Cmcm disordered orthorhombic structure (space group No.63), respectively.

However, the ordered orthorhombic structure of α'' could not be sufficient to explain the strong different intensity contrast between $(021)_{\alpha''}$ and $(001)_{\alpha''}$ in Fig. 1b unless the transverse lattice modulation is taken into account. The $\{1\bar{1}0\}\langle 110\rangle$ -type transverse lattice shuffle is extensively found in the stress-induced phase transformation of β -type titanium alloys [21, 29, 33]. Fig. 8 shows a schematic diagram, which reveals the corresponding relationship between β and α'' phases and the $\{1\bar{1}0\}\langle 110\rangle$ -type transverse displacement. The intensity of $(021)_{\alpha''}$ signal derives from both ordered crystallographic structure and lattice modulation, while the $(001)_{\alpha''}$ signal only depends on the atomic occupation order. However, in our case, the δ phase is not

involved with $\{1\bar{1}0\}\langle 110\rangle$ -type lattice modulation because of the fact that the $(021)_{\alpha''}$ peak is too narrow to conceal the existence of broad δ phase peak if it is really exist (Fig. 2a). The different lattice modulation scenarios in α'' and δ phases could be explained by the heterogeneity of phonon softening [34-36] in their corresponded parent phase, and will discuss in the following sections.

4. Discussion

4.1 The origin of non-uniform chemical compositions in the initial microstructures

There is a coherent decomposition of a homogeneous parent bcc phase, i.e. ordered B2 coherent precipitates in the disordered austenite bcc matrix, which could be attributed to the spinodal decomposition followed by B2 ordering in the Nb-rich domains [37] or the pseudo-spinodal decomposition mechanism which starts by the formation of a nanodomain precursor state with congruent ordering [38, 39]. The low-symmetry α'' phase as a precursor state embedded coherently in the B2 phase could be produced by the local lattice distortion due to point defects such as substitutional alloying elements (Nb, Sn, Zr) with different atomic sizes from the host atoms (Ti). The phase separation of B2 clusters, α'' particles and bcc matrix proves a nanostructured state of the gum-like Ti2448 alloy in the initial microstructure.

4.2 The confined dual-martensitic transformation mechanism at RT

The diffraction spots for α'' martensite always appears ahead of those for δ

martensite (Figs. 3d-3e), which indicates that the formation of α'' and δ martensites does not occur simultaneously in the same stress or temperature environment and the transformation energy barriers for two kinds of martensite are different. The reason on different transformation kinetics for α'' and δ could be explained by local difference in e/a ratio for corresponding B2 and bcc parent phases, i.e. 4.22 and 4.15, respectively. Although some works [40] believe the shear modulus C' of bcc metals increase with an increase in e/a , there are still some peculiar alloy systems disobeying this rule. For example, the number of e/a ratio in GMs is approximately 4.24, which leads to a shear modulus C' almost equal 0 [4, 5]. The Ti-Nb-Ta-Zr-O alloys researched by the group of Tane [41] also finds lower C' at relative higher e/a ratio. Therefore, it could be concluded that the e/a ratio of 4.24 proposed by Satio [3] is indeed anomalous in the influence of shear modulus C' . In our case, the e/a ratio for B2 phase (4.217) is larger than that for bcc (4.15), but B2 phase is more unstable than bcc phase for triggering the martensitic transformation under either stress or temperature field. It indicates that the bcc phase with e/a ratio close to a small range of 4.24 is anomalous in elastic stability and is more unstable than the matrix with e/a ratio far from 4.24.

Meanwhile, another common phenomenon found in the martensitic transformation, i.e. the transverse lattice modulation, also depends on the instability of parent crystal lattice. In our case, we have proved that the $\{1\bar{1}0\}\langle 110\rangle$ -type lattice modulation exists in the phase transformation of α'' phase, but disappears in the δ phase at RT. Moreover, as seen from the evolution of $(220)_\beta$ diffraction spot shown in in Figs. 3c-3f, the diffraction spots finally integrate to be one spot for α'' phase, but still remain

separated for the δ phase. It could also verify the existence of different lattice modulation modes in two kinds of martensites. This is due to the integration of diffraction spots in 3D reciprocal space from two spots into one may be explained by the influence of lattice modulation on the unit cell parameters (lengths and angles) and, finally, leads to the slight orientation switch from martensitic multi-variant into single variant.

However, although the shear modulus could be qualitatively characterized by c/a ratio, the physical origin on softening of shear modulus during the martensitic transformation is still controversy. It has been extensively suggested that the phonon softening mechanism [34-36] is the origin of anomalous phenomena in the martensitic transformation, such as the softening of elastic shear modulus [34, 42], the transverse-type lattice modulation [33, 43] and the appearance of weak diffuse scattering [43-44]. The phonon softening has been widely found in martensitic phase transformation for various alloy systems [34-36], and the phonon softening has a close relationship with the chemical composition, i.e. c/a ratio. Therefore, the different transformation kinetics including different lattice modulation modes for both α'' and δ phases could be explained by the heterogeneity of phonon softening modes due to the inhomogeneous compositions in the corresponding local difference in short-range order structures, such as B2 and bcc, in the parent phase.

It has been proposed that the interstitial alloying elements such as oxygen are responsible for the instability of parent crystal lattice and lattice modulation behavior [21]. In the oxygen-added β -Ti alloys, it was observed six randomly distributed variants

of nanodomains due to six kinds of $\{1\bar{1}0\}\langle 110\rangle$ types lattice modulation in β phase. The added oxygen element made the parent matrix unstable through the local strain fields, which decreased the elastic shear modulus C' . However, in our studied Ti2448 alloy, the low content of oxygen could not form adequate $\{1\bar{1}0\}\langle 110\rangle$ lattice modulation as evidenced by the weak diffuse scattering signal (see the Fig. 1a), which is different from the strong diffuse scattering signals observed in the initial microstructure for the oxygen-added β -Ti alloys [29]. Actually, the doping of substitutional atoms and processing method [12] could lead to the nano-scaled inhomogeneous compositions (Fig. 7b). The B2 clusters with the segregation of heavy atoms are potentially easy to have the phonon softening than the bcc matrix when subjected to external stress. Therefore, the heterogeneity of phonon softening in two phases is more reasonable to explain different transformation behaviors in α'' and δ martensites at RT.

The confined martensitic transformation with the nano-domain-shaped morphology has great contrast with stress-induced normal martensitic transformation with self-accommodating ploytwinned morphology. The frustrated martensitic transformation has also been reported in Ti-Ni-based alloys [26-28]. It has been suggested that the doping of point defects beyond a critical content would result in strain glass state, i.e. the formation of frustrated martensite. However, in our alloy system, the doping of substitutional alloying elements contributes to the phase separation with a nanostructured state in parent phase, i.e. B2 nano-clusters, nano-scaled α'' particles and bcc matrix. Actually, due to the nano-scaled distribution of

inhomogeneous parent phases (B2 and bcc) (Fig. 7b), the inherited sizes of martensitic nanodomains for α'' and δ are restricted to ~ 8 nm and ~ 3.4 nm respectively. The interaction between α'' and δ phases due to their different properties, such as different crystallographic structures, different lattice parameters and the existence of lattice modulation, prevents the growth of nanodomain variant by other nanodomain variants as local barriers [21, 29].

4.3 The martensitic transformation mechanism at 190 K

When the external stimulations (temperature and stress) imposed on the unstable cubic parent phase simultaneously, the cubic parent phase tends to become more unstable. As demonstrated in Figs. 6d-6f, the intensity of separated diffraction spots of δ phase becomes weak with the increase of stress, and the diffraction spots of α'' and δ phases finally merge together, which is in sharp contrast with the separated δ diffraction spot at RT (Fig. 3f). It is reasonable to deduce that the small difference of lattice parameters between α'' and δ phases could be offset by the $\{1\bar{1}0\}\langle 110\rangle$ -type lattice modulation in the δ phase. Therefore, the vanishing of δ spot indicates that, if a $\{1\bar{1}0\}\langle 110\rangle$ -type lattice modulation is triggered in the δ phase, its lattice parameters will become close to that for α'' phase, which indicates that the transformation from δ to α'' may occur by just triggering the lattice modulation by lowering temperature or increasing stress. The uniform lattice modulation in both α'' and δ phases indicates the frozen phonon softening for δ can be broken with decreasing temperature (in the present case at 190 K). The phonon softening further decreases the elastic shear

modulus and induces the transformation from δ to α'' under applied stress.

4.4 The physical origin of anomalous mechanical properties in the Ti2448 alloy

The schematic Temperature-Stress phase diagram (TSPD) for Ti2448 alloy based on our above discussion is sketched in Fig. 9a. The diffraction elastic modulus can be determined by fitting the slope of lattice strain vs. stress at RT and 190K shown in Fig. 2c and Fig. 6. The evolution of the diffraction elastic modulus as a function of stress is displayed in Fig. 9b at different deformation stages.

At RT, the elastic modulus reduces from ~60 GPa to ~30 GPa (O-A stress region) indicating the nonlinear elastic behavior. There are three reversible deformation mechanisms, i.e. nanodisturbances [6], dislocation loops [45] and martensitic transformation [18-20], which are proposed to explain the non-linear elastic behavior. Actually, all of these mechanisms are related to a local shear stress or strain generated in deformation. The difference among them lies in the definition of physical concepts and amount of shear displacement. The arbitrary non-lattice Burgers vector for nanodisturbances is in contrast with quantized Burgers vectors for crystal (full or partial) dislocation, while the amount of localized shear strain for shuffling planes (including lattice modulation) in martensitic transformation is determined by the mismatch of lattice parameters for parent phase and martensite [24]. Besides the localized shear in martensitic transformation, the domain switch from random α'' to oriented α'' martensite in the first two regions in TSPD at RT (Fig. 9a) contributes to the softening of elastic modulus too. The formation of favorable single-variant nanodomains has also

been found in Ti-Ni [28] and Ti-Nb-O [29] alloy systems. We believe that the reversible nano-sized martensitic transformation involving lattice modulation and the switch of oriented variants of martensitic domains is the origin of non-linear elastic behavior.

The co-existence of parent phase and nano-sized α'' martensite region in the TSPD (Fig. 9a) could correspond to the A-B deformation process in Fig. 9b. In this region, the pure shear on the $\{112\}_\beta$ planes to $\langle 111 \rangle_\beta$ directions happens in the Ti-based martensitic transformation, and the large shear strain in the phase transformation contributes to the low elastic modulus in the A-B region and the superelastic behavior. However, with increasing amount of non-modulated phase δ , the boundary effect between the nanodomains of α'' and δ reflects the slow rise of the elastic modulus in the A-B region. When the martensitic transformation completely finished, i.e. the nano-sized α'' and δ martensites co-exist in the region of Fig. 9a, it can be seen that the stress distributed in two kinds of martensites is not uniform, and the average elastic modulus in B-C region shows almost 60 GPa (Fig. 9b).

At the low temperature (190K), the elastic modulus maintains at 13 GPa in the O-A region shown by the red line (Fig. 9b). Due to the extreme instability of single parent phase at the low temperature, the nano-sized α'' martensite had already formed without the process of the switch of orientation martensitic nuclei. Therefore, it is hard to find the nonlinear elastic behavior at the low temperature.

Then with the both stimulation of temperature and stress, the uniform lattice modulation plays a role of the transformation from nano-sized δ martensite to the α'' martensite. The phase region of single α'' phase could be described by the line which

stands for the sign of uniform lattice modulation as a function of temperature and stress in TSPD.

The elastic modulus along tensile direction in A-B region at 190 K is fitted as 48 GPa (red line of Fig. 9b) which is lower than the average elastic modulus at RT (60 GPa). The decrease of elastic modulus also proves the formation of single α'' martensite due to the vanished interplay between nanodomains of α'' and δ phases as local barriers.

It is reasonable to conclude that the high strength of Ti2448 alloy is associated with the interaction between confined martensitic nanodomains, and the gradual transformation from short-range ordered nanostructure to long-range ordered microstructure can promote plastic behavior owing to the strain accommodation between different martensitic variants. The new insight into the martensitic transformation could provide new way to design advance functional and structural materials.

5. Conclusion

In-situ synchrotron-based high-energy X-ray diffuse scattering technique was employed to reveal the intrinsic origin of martensitic transformation and anomalous mechanical behaviors in single crystal Ti-24Nb-4Zr-8Sn-0.1O alloy at RT and 190 K. The main conclusions obtained are summarized as follows:

1. Two kinds of nano-sized deformation-induced martensites exhibiting different crystal structures were clearly observed at RT during the uniaxial tensile loading along $[110]_{\beta}$ axis. The formation of different martensites originated from the

nano-scaled heterogeneity in chemical composition in the parent phase as evidenced by the HAADF microscopic observations.

2. The formation of α'' martensite always preceded the stress-induced δ martensite. The $\{1\bar{1}0\}\langle 110\rangle$ -type lattice modulation existed in the transformation procedure from β to α'' , but not involved in the formation of δ martensite at RT.
3. The martensitic transformation scenario at RT was well revealed by tracing the change in diffuse scattering signals near the Bragg diffraction spot of $(220)_\beta$ over the 3D reciprocal space. The domain switch of oriented α'' martensite resulted in the low elastic modulus and non-linear elastic behavior. The nano-sized δ martensite remained co-existence with α'' phase at 490 MPa.
4. At 190 K, the nano-sized α'' martensite was formed before loading. With increasing stress, the nano-sized δ martensite gradually transformed to α'' phase. Only the single α'' martensite existed after the applied stress was increased to 47 MPa.
5. Two kinds of mechanisms, i.e. the switch of oriented martensitic domains and the reversible martensitic transformation at nanoscale involving lattice modulation, contribute to the nonlinear superelastic behavior.

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Table Caption

Table 1. The lattice parameters for three phases, β , α'' , and δ phases determined by HE-XRDS.

Figure Caption

Fig. 1. The High-energy X-ray diffuse scattering (HE-XRDS) patterns for Ti2448 single crystal obtained from the X-ray incident beam along $[001]_{\beta}$ zone axis at (a) 0 MPa, (b) 274 MPa, the solid circles indicates the weak diffuse scattering signals $(021)_{\alpha''}$ for different variant of α'' domains in (a) and (b). (c)-(f) The evolution of enlarged images (as indicated by solid square in (a)) of the $(220)_{\beta}$ spot under the increase of stress. In the micrographs, solid, dash and chain doted lines represent the evolution of diffraction spots for β , δ and α'' phases respectively.

Fig. 2. The 1D HE-XRDS diffraction profile for (a) $(021)_{\alpha''}$ and (b) $(220)_{\beta}$ under different transformation stages. The inset in (a) is volume fraction change of α'' phase as a function of applied stress. The inset in (b) shows the enlarged peak profile for $(220)_{\beta}$ at 490 MPa and the peaks of α'' and δ phases are fitted by red and blue dash lines respectively. (c), the evolution of lattice strain of $(220)_{\beta}$, $(040)_{\delta}$ and $(040)_{\alpha''}$ as a function of tensile stress. (d), the evolution of lattice strain of $(2\bar{2}0)_{\beta}$ as a function of tensile stress.

Fig. 3. The HE-XRDS patterns for Ti2448 single crystal obtained from the X-ray

incident beam along $[1\bar{1}0]_{\beta}$ zone axis at (a) 0 MPa, (b) 202 MPa. (c)-(f) Zooming into the $(220)_{\beta}$ spot as indicated by solid square in Fig. 3a as a function of applied stress. Solid and dash lines represent the evolution of diffraction spots for β and δ phases respectively.

Fig. 4. With increasing tensile stress, the evolution of lattice strain for $(002)_{\beta}$ highlighted in Fig. 3a is displayed in (a) and the change of cell volume is plotted in (b). Schematic of cell volume is defined in the inset of (b).

Fig. 5. HE-XRDS patterns at 190 K for Ti2448 single crystal obtained from the X-ray incident beam along $[1\bar{1}0]_{\beta}$ zone axis at (a) 0 MPa, (b) 317 MPa. (c)-(f) Zooming into the $(220)_{\beta}$ spot as indicated by solid square in Fig. 5a as a function of applied stress.

Fig. 6. The evolution of lattice strain of $(040)_{\alpha''}$ spot as a function of applied stress at 190 K. The inset shows the evolution of 1D diffraction profile of $(220)_{\beta}$ spot located in Fig. 5a.

Fig. 7. (a) The HAADF-STEM image with the electron beam along the $[100]_{\beta}$ zone axis, the nanodomain structures of Ti-rich and Nb-rich are indicated by solid and dash circles, respectively. (b) The corresponding dark field image from $(110)_{\alpha''}$ electron diffraction pattern in the inset of (b) shows the random distribution of the nanodomain structures.

Fig. 8. A schematic map to show the lattice correspondence between β and α'' phases and the corresponding transverse lattice displacement.

Fig. 9. (a) The schematic Temperature-Stress phase diagram (TSPD) for Ti2448 alloy.
(b) The evolution of elastic modulus along the tensile direction as a function of applied stress at room temperature and 190 K.

$T \sim 298 \text{ K}$

Increasing tensile stress

↑ $110 //$ tensile direction
 ⊗ $(001)_\beta //$ X-ray beam
 → transverse $(\bar{1}\bar{1}0)_\beta$

Fig .1

Fig .2

T~298 K

Increasing tensile stress

↑ 110//tensile direction
 ⊗ (110) $_{\beta}$ // X-ray beam
 → Transverse 002

Fig .3

Fig .4

T~190 K

Increasing tensile stress

↑ 110//tensile direction
 ⊗ Transverse 002
 $(1\bar{1}0)_{\beta}$ // X-ray beam

Fig .5

Fig .6

Fig .7

Fig .8

Fig .9

Table 1. The lattice parameters for three phases, β , α'' , and δ phases determined by HE-XRDS.

Phase	a (Å)	b (Å)	c (Å)
Nano-sized α'' martensite	3.222	4.788	4.667
Nano-sized δ martensite	3.190	4.762	4.680
β	3.298	3.298	3.298