Fatigue properties of a metastable β-type titanium alloy with reversible phase transformation

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Abstract

Due to recent concern about allergic and toxic effects of Ni ions released from TiNi alloy into human body, much attention has been focused on the development of new Ni-free, metastable β-type biomedical titanium alloys with a reversible phase transformation between the β phase and the α' martensite. This study investigates the effect of the stress-induced α' martensite on the mechanical and fatigue properties of Ti–24Nb–4Zr–7.6Sn (wt.%) alloy. The results show that the as-forged alloy has a low dynamic Young's modulus of 55 GPa and a recoverable tensile strain of ~3%. Compared with Ti–6Al–4V ELI, the studied alloy has quite a high low-cycle fatigue strength because of the effective suppression of microplastic deformation by the reversible martensitic transformation. Due to the low critical stress required to induce the martensitic transformation, it has low fatigue endurance comparable to that of Ti–6Al–4V ELI. Cold rolling produces a β + α00 two-phase microstructure that is characterized by regions of nano-size β grains interspersed with coarse grains containing α' martensite plates. Cold rolling increases fatigue endurance by ~50% while decreasing the Young's modulus to 49 GPa along the rolling direction but increasing it to 68 GPa along the transverse direction. Due to the effective suppression of the brittle iso-thermal α phase, balanced properties of high strength, low Young's modulus and good ductility can be achieved through ageing treatment at intermediate temperature.

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1. Introduction

Metallic biomaterials have been widely used to replace failed hard tissues, such as artificial hip joints and dental implants. Compared with stainless steel and Co-based alloys, titanium and its alloys have become one of the most attractive classes of biomedical implant materials due to their advantages of good biomechanical and biochemical compatibilities. Recent research has attempted to overcome the long-term health problem caused by the release of toxic ions from implanted materials and the so-called “stress shielding” effect related to the still too large elastic modulus of materials as compared with that of the surrounding hard tissue. Novel titanium alloys with greater biocompatibility, lower elastic modulus and better processability are desirable.

α + β-type titanium alloys composed of non-toxic elements, such as Ti–5Al–2.5Fe and Ti–6Al–7Nb, were among the first to be developed for biomedical applications [1,2]. These alloys, however, are still too stiff compared with human bone and may lead to premature failure and/or loosening of the implant due to stress shielding. Because the body-centred cubic (bcc) β phase has much lower elastic modulus than the hexagonal close-packed (hcp) α phase, a series of near-β and metastable β-type titanium alloys containing only non-toxic elements such as Nb, Ta, Zr and Mo have been developed [3–7].

Besides its low elastic modulus, the shape memory effect of the β phase has also been exploited, taking advantage of the reversible β to α' martensitic transformation [8,9]. The limitation of very fast heating rate for shape recovery, how-
ever, discouraged systematic investigations for functional applications. Recently concern about the allergic and toxic effects of Ni ions released from TiNi alloy led an increase in attention paid to the development of new Ni-free shape memory titanium alloys, such as Ti–Nb–Sn [10], Ti–Mo [11] and Ti–Nb [12]. These alloys invariably exhibit the so-called “double yielding” phenomenon during tensile testing, of which the first “yielding” corresponds to the critical stress needed to induce \( \alpha'' \) martensitic transformation from the parent \( \beta \) phase. Since chemical compositions of metastable \( \beta \)-type titanium alloys with low elastic modulus are located generally in the chemical ranges of stress-induced martensitic transformation, the exceptionally low strength of the first “yielding” raises concern over the endurance life of implants made of such materials in the human body.

By adjusting the \( \beta \) phase stability through Nb addition and suppressing the martensitic transformation through alloying with both Zr and Sn, a new \( \beta \)-type titanium alloy, Ti–24Nb–4Zr–7.9Sn (wt.%) was developed [13–16]. This alloy exhibits unusual features in both the elastic and plastic deformation regimes: stress–strain curves have a continuous skewing shape with no apparent yielding point, and a maximum recoverable strain up to 3.3% and low elastic modulus matching that of human bone can be achieved by slight pre-straining. At high plastic strain, cold rolling for example, the alloy undergoes highly localized deformation which refines coarse grains to tens of nanometers, but little increase in tensile strength is observed. Because reversible martensitic transformations also cause large-scale superelasticity and significant grain refinement, as demonstrated by the well-known NiTi-based shape memory alloys [17], it is necessary to examine the relation of the \( \alpha'' \) martensite to the peculiar deformation behaviours mentioned above and to mechanical properties.

It is known that 1 wt.% of Sn decreases the martensitic start temperature by \( \sim 41 \) °C in the quaternary Ti–Nb–Zr–Sn alloy [14], so 7.6Sn instead of 7.9Sn is preferred in the present study in order to induce the \( \alpha'' \) martensitic transformation by raising the phase transformation temperature. Since interstitial oxygen in the bcc crystal improves the phase stability against martensitic transformation, 0.07 wt.% oxygen is adopted in this study instead of the \( \sim 0.11 \) wt.% in previous studies [13,15]. By comparing with Ti–24Nb–4Zr–7.9Sn alloy we hope to understand the role of the reversible \( \beta \) to \( \alpha'' \) martensitic transformation during the elastic and plastic deformation. Due to the lack of life-endurance information of \( \beta \)-type superelastic titanium alloys, the fatigue properties of Ti–24Nb–4Zr–7.6Sn were investigated through tension–tension testing in air and 0.9% NaCl solution.

2. Experimental

An ingot with a diameter of 140 mm was melted three times in a vacuum arc remelting furnace using pure Ti, Nb, Zr and a Ti–Sn master alloy as raw materials. To ensure the chemical homogeneity of the melted ingot, it was hot-forged at 1000 °C after the second melting, then machined and melted again. The actual composition of the alloy obtained by wet chemical and gas analysis is shown in Table 1. The ingot was hot-forged at 1000 °C and then at 850 °C into a round bar, 25 mm in diameter, and a billet, 30 mm in thickness. The billet was hot rolled at 850 °C into a slab with a thickness of 7 mm, and then cold-rolled into a 2.0 mm sheet with thickness reductions of \( \sim 70\% \) without intermediate annealing. The hot-forged Ti–6Al–4V ELI used in this study was supplied by Baoji Non-ferrous Metals Works of China.

The forged and heat-treated specimens were machined to the dimensions given in Fig. 1(a) for tensile tests. Some

![Fig. 1. Geometries of (a) tensile, (b) high-cycle fatigue (c) low-cycle fatigue specimens for hot-forged alloy, and (d) tensile and high-cycle fatigue specimens for cold-rolled sheets employed in this investigation (unit: mm).](image-url)
plate specimens, with a rectangular cross-section of 3.0 mm × 2.0 mm and a gauge length of 13 mm for tensile tests, were machined from the cold-rolled sheets with their longitudinal directions parallel to the rolling direction. The tensile test was conducted at room temperature (21 °C) by cyclic loading–unloading deformation at an initial strain rate of 1.3 × 10⁻⁴ s⁻¹ using an Instron-type machine, with a strain gauge being used to record the stress–strain curves. To improve accuracy, the reported tensile properties are the average of two individual tests. Vickers hardness was measured using a hardness tester with a load of 100 g held for 15 s and 10 points were measured to obtain an average value.

The fatigue properties of the specimens were evaluated using an electro-hydraulic-servo testing machine. For the high-cycle fatigue test controlled by applied stresses, the round specimens (Fig. 1b) were used for the hot-forged round bars while the plate specimens (Fig. 1d) were used for the cold-rolled sheets. For the low-cycle fatigue test controlled by applied strains, the plate specimens (Fig. 1c) were prepared from the hot-forged round bars according to Chinese standard GB 15248-94 to save the test materials. In order to avoid any notches that may form during the machining process, the specimens were ground with SiC papers from 57 to 10 μm and then polished. The surface roughness of the fatigue tested specimens was ~300 nm, as measured by a surface topography tester. The high-cycle fatigue tests were conducted at a stress ratio, R, of 0.1, a frequency of 30 Hz and a sinusoidal cyclic waveform in air and in a 0.9% NaCl solution at room temperature. To ensure the fatigue endurance of the tested materials, the fatigue limit was determined by two individual specimens without fracture during the high-cycle fatigue test. The low-cycle fatigue tests were conducted at a strain ratio, R, of 0.1, a frequency of 0.5 Hz and with a triangular cyclic waveform in air at room temperature under total strain control.

The dynamical Young’s modulus was measured by a free resonant vibration method at ambient temperature according to Chinese standard GB/T2105-91 using cylinders 8 mm in diameter and 180 mm in length or plates 150 × 10 × 2 mm³ in dimension (with their length in both the rolling and perpendicular directions) [16]. The method has maximum system errors of less than ±1%. Instead of the dynamical Young’s modulus, the tensile Young’s modulus was measured for those heat-treated specimens to save the test materials. In order to improve accuracy, a strain gauge being used to record the stress–strain curves. Comparing the tensile Young’s modulus with the dynamical Young’s modulus and examining the deviations of measurement from two individual specimens showed that the tensile Young’s modulus had an error of less than ±3% of the actual value.

Phase constitutions were examined with an X-ray diffractometer (XRD) using a Cu Kα radiation source with an accelerating voltage of 40 kV and a current of 250 mA. The microstructures were observed with a LEO SUPRA35 scanning electron microscope (SEM) and a JEOL 200 CX-II transmission electron microscope (TEM) operating at 200 kV. Specimens for SEM observation were etched at the boiling temperature of a water solution with 40 vol.% HCl. Samples for TEM analysis were prepared by twin-jet electropolishing in a solution of 60 ml perchloric acid, 85 ml n-butanol and 150 ml methanol at temperatures between −35 and −25 °C.

3. Results

3.1. Microstructure and phase constitution

Fig. 2 shows microstructures of hot-forged and cold-rolled Ti–24Nb–4Zr–7.6Sn alloy (hereafter denoted 7.6Sn alloy). It is clear from SEM photograph (Fig. 2a) that the hot-forged bar consists of equiaxed β grains with a cross-section size of ~5 μm. However, TEM observation found the equiaxed β grains to be divided into a great number of sub-grains with sizes less than 1 μm (Fig. 2b). Consistent with our previous investigation, diffraction analysis failed to detect diffuse scattering and reflection contributed by the ω phase in the hot-forged specimen (inset of Fig. 2b). TEM analysis of the cold-rolled sheet showed partial nanostructuring, as evidenced by the continual diffraction rings of the β phase (inset of Fig. 2c). However, cold rolling with a thickness reduction of 70% is not sufficient to produce homogeneous nanostructuring: regions of coarse grains (top right) co-exist with nanostructured regions (bottom left,) as shown in Fig. 2d. The grain refinement was also confirmed by XRD analysis, which revealed significant broadening of the diffraction peaks of the cold-rolled sheet as compared with the hot-forged bar (Fig. 3). XRD analysis also showed that the cold-rolled sheet has a β + γ' two-phase microstructure. An optical micrograph of the hot-forged Ti–6Al–4V ELI is given in Fig. 2f, showing that the alloy consists mainly of equiaxed grains, with only a little amount of lamellar microstructure.

It has been reported that martensitic plates resulting from stress-induced phase transformation favour grain refinement during cold deformation [18]. Our recent study, however, found that an alloy with higher Sn content (7.9 wt.% instead of 7.6 wt.% to suppress the martensitic transformation) exhibits more pronounced grain refinement than the present alloy during compression testing [13]. This is further supported by the following TEM observation. Fig. 2(e) shows that the 60 nm thick α’ martensite plate at the centre has not been refined during cold rolling with 70% thickness reduction.

After the hot-forged alloy was aged between 350 and 500 °C at intervals of 25 °C, XRD analysis (Fig. 3) and TEM observations (Fig. 4) did not detect the formation of ω phase with ageing time up to 48 h. This gives further evidence that both the athermal and isothermal ω phases are suppressed in the studied quaternary alloy, in sharp contrast with previously reported metastable β-type titanium alloys. SEM observations showed that the α phase...
precipitated during ageing treatment appears to have a needle-like shape and becomes finer with decreasing ageing temperature (Fig. 5).

3.2. Superelasticity

The hot-forged Ti–24Nb–4Zr–7.6Sn alloy was subjected to cyclic tensile loading to a total strain of 5% at an interval of 1% (Fig. 6). It is clear that the elastic strains of 1, 2 and 3% are fully, almost fully and largely recovered, respectively, during unloading. The recoverable strain is slightly lower than the alloy with 7.9 wt.% Sn [13]. Since the stress–strain curves in Fig. 6 exhibit the so-called “double yielding” phenomenon, in which the first “yielding” corresponds to the critical stress to induce $\alpha''$ martensitic transformation from the parent $\beta$ phase, there is little doubt that the superelasticity of this alloy is mainly related to the reversible $\beta$ to $\alpha''$ transformation. This was further supported by the large amount of $\alpha''$ martensite obtained by cold rolling (Fig. 3).

3.3. Young’s modulus and tensile properties

The dynamical Young’s modulus measured by the resonance method of the hot-forged alloy is $\sim$55 GPa. After cold rolling, it decreases to 49 GPa along the rolling direction and increases to 68 GPa along the transverse direction due to the formation of a rolling texture. These results are consistent with the tensile Young’s modulus determined from the stress–strain curves recorded with a strain gauge. The tensile properties of the hot-forged and cold-rolled 7.6Sn alloys as well as the Ti–6Al–4V ELL alloy are listed in Table 2.

Variations of Vickers hardness of the hot-forged alloy with ageing temperature and time are shown in Fig. 7. Between 400 and 450 °C, the hardness increases rapidly with ageing time up to 4 h, gradually increases further up to 24 h and then remains almost constant up to 48 h. Such an age-hardening effect is in contrast with the previously reported metastable $\beta$-type titanium alloys. For example, after ageing below 450 °C in the ($\alpha + \beta + \omega$) three-phase
or \((\beta + \alpha)\) two-phase field, the Vickers hardness of Ti–29Nb–13Ta–4.6Zr alloy increases gradually with ageing time up to 48 h \[19\]. Since the \(\alpha\) phase grows at the expense of the \(\omega\) precipitation \[20\], this barrier effect, together with the sluggish kinetics of the \(\omega\) precipitation from the \(\beta\) phase, results in the lack of rapid hardening during the early stage ageing, in contrast with the present alloy without the formation of the \(\alpha\) phase. Fig. 7 also shows that 4 h between 450 and 500 °C will result in overageing, as proved by the slow decrease in hardness with increasing ageing time.

Biomedical applications to replace disfunctional hard tissue require a balance of high strength and low elastic modulus in order to achieve a long service life of the implants and to minimize the “stress shielding” effect. Ageing treatment of the studied alloy between 350 and 500 °C increases both the strength and the Young’s modulus, and decreases the ductility due to the formation of the \(\alpha\) phase (Fig. 8). In spite of the negative effect of the \(\alpha\) phase on the elastic modulus, a yield strength of \(\sim 1000 \text{ MPa}\) can be reached at a Young’s modulus of \(\sim 75 \text{ GPa}\) after ageing at 400 °C for 4 h.

### 3.4. Fatigue properties

Fatigue resistance is one of the most important mechanical performances for structural biomaterials because, in general, biomaterials are used under cyclic loading conditions. In this work, the fatigue properties of the hot-forged, cold-worked and aged 7.6Sn alloy were evaluated using a tension–tension test in air and 0.9% NaCl solution (Fig. 9).

#### 3.4.1. Stress-controlled fatigue life

The fatigue endurance limit of the hot-forged alloy is similar to that of CP Ti but lower than that of Ti–6Al–
The fatigue lifetime of hot-forged 7.6Sn alloy is slightly higher in 0.9% NaCl than that in air in the low-cycle regime. Ageing treatment at 400°C for 4 h increased the fatigue limit of the 7.6Sn alloy to more than 425 MPa, which is comparable to the fatigue limit of Ti–6Al–4 V ELI. The increase in fatigue strength is due to the improvement of the strength caused by the precipitation of very fine α phase during ageing (Fig. 4a), which leads to increased resistance to the fatigue crack initiation and small fatigue crack propagation [6].

The fatigue resistance of the cold-rolled sheets is increased by ~50% over the hot-forged bars (Fig. 9). SEM observation found that the cold-rolled alloy exhibits a ductile fatigue fracture morphology similar to that of the hot-forged alloy (Fig. 10). Additionally, the fast fracture area of the cold-rolled alloy occupies most of the fracture surface. It has been reported that, for titanium alloys with
from the nomenon contributed by the reversible transformation. The kind of alloys exhibiting the “double yielding” phenomenon (Fig. 9) raises concern about load-bearing applications of microstructures produced by cold rolling. The low fatigue strength of the as-forged 7.6Sn alloy is mainly due to the increase in the resistance against fatigue-crack initiation caused by the much finer microstructures, a large part of the fatigue life is occupied by the small fatigue crack initiation and relatively fine microstructures, a large part of the fatigue life is occupied by the small fatigue crack initiation and propagation life [22]. Therefore, it can be deduced that the improvement of the fatigue resistance of the cold-rolled 7.6Sn alloy can take place in two ways: to depress the stress-induced phase transformation and propagation life. Due to the sluggish transformation from the β phase to the α′ martensite, in particular the previously reported alloys which require lower critical stress to induce phase transformation. To keep the merit of the low elastic modulus of such alloys, cold-processing techniques such as rolling and swaging would be reasonable options to improve fatigue properties. For example, cold rolling results in a fatigue strength of ~375 MPa (Fig. 9). Another way is to depress the stress-induced phase transformation by chemical composition design. For the studied Ti–Nb–Zr–Sn system, a lower elastic modulus and a larger recoverable strain were achieved by increasing both the Sn and oxygen contents [13,15]. Additional fatigue testing showed that the fatigue strength can be increased by 50–100 MPa from ~250 MPa for the studied alloy.

3.4.2. Strain-controlled fatigue life

Strain-controlled low-cycle fatigue (LCF) properties of hot-forged 7.6Sn alloy and Ti–6Al–4V ELI were investigated at a strain ratio, R, of 0.1 and a frequency of 0.5 Hz in air at room temperature. The maximum cyclic strains are plotted as a function of the number of cycles to failure, and a linear relation is obtained for both alloys (Fig. 11). Compared with Ti–6Al–4 V ELI, the 7.6Sn alloy shows a much higher fatigue resistance in the strain-controlled fatigue test. Especially for cyclic strains between 0.25 and 2.5%, the 7.6Sn alloy can take ~4 × 10⁶ cycles to failure, whereas the Ti–6Al–4V ELI takes ~6 × 10⁵ cycles.

The cyclic stress–cycle curves of the 7.6Sn alloy are shown in Fig. 12. It can be seen that, at low strains of less than ~3.5%, there exists obvious cyclic hardening after the initial cyclic softening whereas continual softening happens at high strains above ~4.0%. For Ti–6Al–4V ELI, there is only softening behaviour without hardening under the studied strain ranges larger than ~2.5%, which is well beyond its elastic limit of ~0.6%. Since the LCF test induces two kinds of transformations in the 7.6Sn alloy, as shown in Section 4, this results in complicated cyclic softening and/or hardening behaviour.

Fig. 13 gives an example of the recorded hysteresis loops of the 7.6Sn alloy and Ti–6Al–4V with a maximum strain of ~2.5%. It can be seen that the plastic strain per cycle of the 7.6Sn alloy is much smaller than that of Ti–6Al–4V ELI and the recorded hysteresis loop per cycle of the former alloy is not symmetrical. The cycle numbers to failure (Nf) and the plastic strain per cycle (Δεp) of both alloys can be fitted to the Coffin–Manson equation [23]:

\[ N_f \Delta \varepsilon_p = C \]  

in which γ and C are constants related to the elongation to fracture of material in static loading. In the studied strain range, the calculated constants γ and C are respectively 0.46 and 0.22 for the 7.6Sn alloy, which are much lower than for Ti–6Al–4V ELI (0.72 and 1.21, respectively). Low values of Δεp and γ are in agreement with materials exhibiting superelastic deformation behaviour, such as NiTi [24].

4. Discussion

4.1. The formation of α phase

Due to the sluggish transformation from the β phase to the α phase in metastable β-type titanium alloys, the brittle
phase with a high elastic modulus cannot be suppressed in general as it is cooled from a high temperature above the β transus (the athermal ω phase) or aged at low temperatures below ~450 °C (the isothermal ω phase) [19,20]. This is in sharp contrast with the studied alloy, in which both kinds of ω phase are fully suppressed (Figs. 2 and 4).

The ω phase forms generally by collapsing one pair of (1 1 1) planes and keeping the adjacent (1 1 1) planes stable due to the elastic instability of the bcc crystal [25]. Its formation can be hindered by the addition of both alloying elements and interstitial elements such as Zr, Al, Sn and oxygen [26,27]. However, the thorough suppression of the ω phase is quite difficult to achieve through chemical design. For example, in Ti–35Nb–7Zr–5Ta alloy, the ω phase can be fully suppressed by incorporating sufficient oxygen (reaching ~0.5 wt.% [27], which is much higher than the ~0.07 wt.% of the studied alloy. Apart from the oxygen effect, the β phase in the former is more stable according to the relation between the electron/atom ratio and the phase stability established in binary alloy systems [28], and should make the ω formation more difficult. This is contrary to the experimental findings of the present work. Our previous investigations also showed that the formation of the athermal ω is dependent on both the Zr and Sn content in Ti–(20–26)Nb-based alloys, while appropriate amounts of Zr and Sn have the advantage of suppressing the formation of both the martensite and the ω phase [14]. Thus it can be seen that the origin of the ω phase and its suppression in the Ti–Nb–Zr–Sn system are complicated and need further investigation.

Interestingly, TEM analysis found the ω phase in the regions close to the fracture surface after the LCF test, e.g. that of maximum strain ~3% shown in Fig. 14. Since the ω phase is fully suppressed in the studied alloy under the conditions of heat treatments, static tensile tests and cold rolling, it should be related to cyclic strains during the LCF test. Therefore, the observed ω phase should be athermal in nature. The corresponding bright- and dark-field images in Fig. 14 provide strong evidence that the ω phase precipitates appear to decorate dislocation lines and dislocation dipoles (in the latter case, the precipitates tend to appear in pairs; see Fig. 14b) rather than nucleating uniformly. This is distinct from the uniform cuboidal or ellipsoidal morphology as observed in metastable β-type titanium alloys during cooling from high temperature and low temperature ageing. The unindexed diffraction spots in Fig. 14d are due to secondary or double diffractions. Such an athermal ω phase with the peculiar morphology shown in Fig. 14 was also observed in the LCF test specimens with a maximum cycle strain of ~5%, as well as in the HCF test with an applied stress of 600 MPa in NaCl solution. A systematic investigation is underway to reveal the
influence of cycle stress and strain on the athermal ω phase formation.

The Ti–Nb–Zr–Sn quaternary alloys were developed under the inspiration of suppressing the ω phase to achieve an ultralow elastic modulus so as to be close to that of human bone (for details see Fig. 1 in Ref. [15]). It is not clear, however, why the ω phase has been totally suppressed in the hot- and cold-processed alloys as well as the aged alloys. These results at least exclude the possibility that the athermal ω phase observed after cyclic deformation is due to the slight variation in alloy composition. Previous XRD and TEM investigations showed that no ω phase was detected in the quaternary alloys with Sn contents between 7.5% and 8.2% and oxygen in the range of 0.07–0.20%. The chemical composition of the current alloy falls in the above range. Additionally, the athermal ω phase was not observed after conventional tensile testing to fracture at room temperature and after cold rolling. For example, in the cold-rolled Ti–24Nb–4Zr–7.9Sn alloy with thickness reductions above 90%, no ω phase was detected by XRD and TEM analysis even in the aged specimens at temperatures below 450 °C [29]. Thus, the athermal ω phase shown in Fig. 14 should have been induced by the cyclic deformation.

### 4.2. Effect of reversible phase transformation on the strain-controlled fatigue life

It is well-known that the basic factor governing the life endurance at LCF is the elementary microplastic deformation introduced into the material per cycle ($\Delta e_p$), whereas the mechanical property of materials is of only secondary influence [23]. Due to the reversible deformation contributed by martensitic transformation, the $\Delta e_p$ of the 7.6Sn alloy is significantly lower than that of Ti–6Al–4V ELI during the LCF test. Thus, the former has a longer fatigue life than the latter according to Eq. (1). Additionally, the stress relaxation contributed by the reversible martensitic transformation also inhibits the crack nucleation and propaga-

![Fig. 12. Cyclic stress response curves for as-forged Ti–24Nb–4Zr–7.6Sn (a), and Ti–6Al–4V ELI (b) at different maximum strains (in percent).](image)

![Fig. 13. Hysteresis loops of as-forged Ti–24Nb–4Zr–7.6Sn (a), and Ti–6Al–4V ELI (b) recorded at different cycles of maximum strain 2.5% during the LCF test.](image)
tion [24,30,31]. As a result, the 7.6Sn alloy has better LCF properties than Ti–6Al–4V ELI, as shown in Fig. 11.

During the LCF test with the maximum strains beyond the range that can be fully recovered, cyclic plastic deformation results in slip bands, the $\alpha''$ martensite and the athermal $\omega$ phase (Figs. 14–16). The formation of both the slip bands and the unrecoverable $\alpha''$ martensite is dependent on the applied strains during the LCF test. SEM observation of the lateral surface close to fracture areas found that the maximum strain of $\sim 3.5\%$ is the critical strain amplitude to induce slip bands. Slip bands are formed easily above this value but are rarely observed below it, as shown in Fig. 15 for the maximum strains of 4.5% and 2.5%. XRD analysis also showed that the volume fractions of the unrecoverable $\alpha''$ martensite decrease with decreasing applied strains (Fig. 16). Since the amount of the athermal $\omega$ phase is too little and below the detecting limit of XRD analysis (Figs. 14 and 16), the influence of the amplitude of the cyclic strain on its formation is not yet defined.

The slip band mechanism is one of the main reasons for cyclic softening by producing easy paths for subsequent damage accumulation [32], thus there is only cyclic softening under the condition of maximum strains above 3.5%. The rapid drop in the cyclic stress, in particular during the later stage of cycling, is due to the fast propagation of cracks resulting from the intense planar slips [33]. Another softening mechanism is the decrease of phase stability originating from internal stresses, which are introduced by cyclic plastic deformation. This is in agreement with the increase in the martensitic transformation temperature of the specimen surface after mechanical polishing [14]. The cyclic softening of the LCF test (Fig. 12) can be explained by both mechanisms at high strains above.

![Fig. 14. Microstructure of the athermal $\omega$ phase formed near the fracture surface of as-forged Ti–24Nb–4Zr–7.6Sn after an LCF test with maximum strain of 3%, in which (a) and (b) are a pair of bright- and dark-field TEM images, (c) is selected area diffraction pattern and (d) its index.](image)

![Fig. 15. SEM micrographs of as-forged Ti–24Nb–4Zr–7.6Sn close to the fracture surface after LCF tests with maximum strains of 4.5% (a) and 2.5% (b).](image)
5. Conclusions

The influence of stress-induced \( \alpha'' \) martensite on the mechanical and fatigue properties of a metastable \( \beta \)-type titanium alloy with a chemical composition of Ti–24Nb–4Zr–7.6Sn (wt.%) was examined and the main findings are as follows:

1. The as-forged alloy with a single \( \beta \) phase has a low dynamic Young’s modulus of \( \sim 55 \) GPa and a recoverable tensile strain of \( \sim 3\% \), the superelasticity largely being due to the reversible phase transformation between the \( \beta \) phase and the \( \alpha'' \) martensite.

2. Due to the suppression of microplastic deformation by the reversible phase transformation, the studied alloy exhibits a high low-cycle fatigue strength and a low fatigue endurance comparable to that of Ti–6Al–4V ELI.

3. The studied alloy exhibits a significant age-hardening effect during short-time ageing at low temperature. Due to the effective suppression of the brittle isothermal \( \omega \) phase, balanced properties of high strength, low Young’s modulus and good tensile ductility can be achieved through ageing treatment.

4. Cold rolling produces a \( \beta + \alpha'' \) two-phase microstructure. At a thickness reduction of 70\%, a mixture of refined regions containing nano-size grains of the \( \beta \) phase and coarse \( \beta \) grains containing \( \alpha'' \) martensite results.

4.3. Effect of environment on fatigue life of hot-forged Ti–24Nb–4Zr–7.6Sn

As shown in Fig. 9, the fatigue cycles to failure of the as-forged 7.6Sn alloy in 0.9% NaCl solution are larger than that in air at high stresses between 350 and 700 MPa, whereas the fatigue strength at the endurance limit of \( 10^7 \) cycles is almost identical, at \( \sim 250 \) MPa, in both environments. Such a phenomenon can be explained as follows: one factor is the increase of temperature during fatigue test, in particular for materials with high damping properties due to reversible martensitic transformation as well as under high-cycle stress condition. Since the NaCl solution has the advantage of cooling specimens, it is more efficient to suppress material softening originating from the temperature increase. The above phenomenon is also consistent with previous experimental findings of the well-known NiTi shape memory alloys [36, 37]. The second factor would be passive oxide film formed in NaCl solution. According to the passivity theory, the passive oxide layer formed on titanium alloy is active and passive simultaneously when in contact with electrolytes [38, 39]. During the cyclic fatigue test, surface deformations such as slip bands, intrusions and extrusions or microcracks will appear, leading to an oxide film rupture and a local loss of passivity [40]. If the destroyed passive oxide cannot be reprecipitated sufficiently, it will accelerate the corrosion behaviour of materials and do harm to the HCF life in corrosive solutions [41]. In this case, the oxide films with higher toughness and ductility will be of greater benefit for the fatigue properties of materials compared with brittle oxide films [40]. Since Nb_2O_5 and ZrO_2 exhibit good passivity and are not prone to chemical breakdown in solution [42, 43], both ductile oxides reduce the negative effect of the corrosion environment during fatigue and improve corrosion fatigue resistance as compared with brittle passive titanium oxide.

3.5%, but only by the mechanism of elastic softening at low cyclic strains. The athermal \( \omega \) phase would contribute to cyclic hardening because it is in general harder than the \( \beta \) phase [19]. However, such a strengthening effect would be very weak considering only the small amount of \( \omega \) phase formed during the fatigue cycles, which is below the detecting limit of XRD measurement.

The cyclic hardening observed in Fig. 12 is difficult to understand. The unrecoverable martensite due to the accumulated microplastic deformation is a possible reason, as evidenced by cyclic hardening in stainless steel with the aid of the stress-induced martensitic transformation [34, 35]. However, Fig. 16 shows that the volume fractions of the unrecoverable \( \alpha'' \) martensite decrease with decreasing applied strains. This suggests that the hardening effect would weaken with decreasing cycle strains if unrecoverable martensite is the dominating cause of hardening. By contrast, the experimental results show continuous softening at high-cycle strains larger than \( \sim 3.5\% \) as well as softening and then hardening at low-cycle strains (Fig. 12). Furthermore, the martensite in the studied system has a much weaker contribution to hardening than that in stainless steels [13].
(5) Cold rolling increases the fatigue endurance by ~50%. The Young's modulus decreases to 49 GPa along the rolling direction and increases to 68 GPa along the transverse direction.

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References


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