Nonlinear elastic deformation behaviour of Ti–30Nb–12Zr alloys

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We report the nonlinear elastic deformation behaviour of Ti–30Nb–12Zr alloys containing varying amounts of oxygen and/or nitrogen. These alloys feature an electron/atom (e/a) ratio of ~4.19, in between the e/a values of two groups of multifunctional titanium alloys reported previously (Gum Metal ~4.24 and Ti2448 ~4.15), and thus demonstrate an independence of the nonlinear elasticity on the e/a ratio. This study also found that the nonlinear elasticity persists in this type metastable β titanium alloys regardless of the presence of a small amount of other phases such as α, α′ and ω.

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The electron/atom (e/a) ratio is a crucial parameter that characterizes the elastic stability of body-centred cubic (bcc) crystals [1]. Experimentally it was found that the lower the e/a ratio, the lower the elastic modulus of metastable β-type titanium alloys [1,2]; the e/a ratio is therefore widely quoted in the pursuit of low elastic modulus [3,4]. The softening mechanism provided by the stress-induced martensitic transformation (MT) in this class of materials is unfavourable in this regard, because this mechanism does not meet the demand of a relatively high strength [5]. The generally reversible MT [1,6], however, was used together with the control of the e/a ratio to design β-type shape memory alloys for biomedical applications [7], in an attempt to overcome the allergic effect of NiTi alloys.

Two groups of metastable β-type titanium alloys with improved balance of high strength and low elastic modulus have been developed. One is the so-called Gum Metal with e/a ratio of ~4.24 [8,9], falling in the range specified for biomedical titanium alloys with low elastic modulus [3,4]. Another is Ti2448 (Ti–24Nb–4Zr–8Sn in wt.%) with e/a ratio of ~4.15 [10,11]. Both alloys exhibit peculiar deformation behaviour of nonelasticity and highly localized plasticity [8–11] in spite of significant differences in composition and processing [12]. A number of deformation mechanisms have been proposed, for example dislocation-free glide and reversible MT for the Gum Metal [8,12–15], extensive lattice distortion for the Ti2448 [16], as well as multiple elastic mechanisms involving lattice distortion, dislocation loops and MT that activate in turn with increasing applied stress for a modified Ti2448 alloy (M–Ti2448) with lower contents of tin and oxygen to promote the stress-induced MT [17,18]. While the origin of the nonlinear elasticity is still far from clear, the evidence so far (in situ tensile tests and fatigue tests [12,16–18]) suggests that elastic mechanisms other than the reversible MT are operating and these mechanisms contribute to the nonlinear elasticity at low stress level.

Nonlinear elastic behaviour found in both the Gum Metal and Ti2448 with distinct e/a values would suggest that such behaviour is typical of a wide range of β-type titanium alloys and is not related to a particular value of e/a. Indeed, alloying effects on the phase stability in these multi-component systems are more complex than can be indexed with a single e/a parameter. For example, Zr and Sn tend to have a weak influence on the stability of the β phase in α-type alloys but have significant effects in Ti–Nb alloys with large amount of Nb additions [7,19]; oxygen, a strong α stabilizer in α- and (α+β)-type alloys, appears to be a β stabilizer in β-type alloys with respect to other metastable phases [1,8].

To verify the above hypothesis that the nonlinear elasticity is not dictated by a narrow range of the e/a ratio, we investigated a group of Ti–Nb–Zr alloys with e/a ratio of ~4.19, roughly half way between that of Ti2448 (~4.15) and the Gum Metal (~4.24). These alloys are based on Ti–30Nb–12Zr (wt.%) and contain varying amounts of oxygen and/or nitrogen. Within
terms of phase constituent, these alloys have either (β + α′ + ω) or (β + α + α′ + ω) phase combination.

Figure 1. XRD profiles of the annealed Ti–30Nb–12Zr alloys with different oxygen contents (a) and nitrogen contents (b).

has maximum systematic error within ±1%. The Vickers hardness was measured under a load of 10 kg applied for 15 s along the longitudinal direction of specimens. Phase constitutions were determined by X-ray diffraction (XRD) analysis using Cu Kα radiation at an accelerating voltage of 40 kV and a current of 250 mA. In order to avoid artifact of the stress-induced MT, the specimens were heavily etched in a water solution of 8 vol.% of HF to remove surface layer with internal stress introduced by grinding and polishing. Specimens for optical microscope observation were etched at the boiling temperature of a water solution with 40 vol.% HCl. The microstructures were observed by transmission electron microscopy (TEM), using a microscope operating at 200 kV. TEM specimens were prepared by twin-jet electropolishing in a solution of 21% perchloric acid, 50% methanol and 29% n-butyl alcohol at about −40 °C.

Phase constitutions of the annealed Ti–30Nb–12Zr alloys with different oxygen and nitrogen contents were characterized by both XRD and TEM analyses and the results are listed in Table 1. From the XRD profiles shown in Figure 1, it is clear that all the studied alloys contain mainly the β phase. The α phase forms in the alloys with nitrogen additions and its volume fraction increases with the increase of nitrogen content. Enlargement of the diffraction peaks shows that all the studied alloys contain a little amount of the α′ martensite, and its volume fraction appears to decrease with the increase of both oxygen and nitrogen content. Optical observations found a dispersion of α phase particles in a β matrix (the dark precipitates in Fig. 2b) but failed to identify the α′ martensite except the alloy free of both oxygen and nitrogen additions. TEM analyses showed that a little amount of both the α′ martensite and the α phase formed in all the annealed alloys, for example the alloys with nitrogen additions of 0.34 and 0.49 wt.% (see the corresponding selected-area diffraction (SAD) patterns of the β matrix in Fig. 2c and d). Because the diffraction spots of both metastable phases are weak, their morphologies cannot be distinguished clearly in dark-field images. Inspection of the SAD patterns showed that their volume fractions appeared to decrease with the increase of interstitial contents. Different from the typical needle-shaped α phase in metastable β-type titanium alloys [1], the α phase in the alloys with high contents of nitrogen additions has much smaller aspect ratios and looks almost equiaxed with size less than 1 μm (Fig. 2d). The observations suggest that

<table>
<thead>
<tr>
<th>O (wt.%)</th>
<th>N (wt.%)</th>
<th>H (wt.%)</th>
<th>Phases</th>
<th>E (GPa)</th>
<th>σu (MPa)</th>
<th>σu/E (%)</th>
<th>δ (%)</th>
<th>Hv (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>0.009</td>
<td>0.006</td>
<td>β + α′ + ω</td>
<td>67.0</td>
<td>545</td>
<td>0.81</td>
<td>48</td>
<td>1.9</td>
</tr>
<tr>
<td>0.20</td>
<td>0.009</td>
<td>0.007</td>
<td>β + α′ + ω</td>
<td>67.4</td>
<td>6755</td>
<td>1.00</td>
<td>37</td>
<td>2.4</td>
</tr>
<tr>
<td>0.29</td>
<td>0.008</td>
<td>0.007</td>
<td>β + α′ + ω</td>
<td>68.2</td>
<td>720</td>
<td>1.06</td>
<td>30</td>
<td>2.7</td>
</tr>
<tr>
<td>0.37</td>
<td>0.010</td>
<td>0.005</td>
<td>β + α′ + ω</td>
<td>68.9</td>
<td>830</td>
<td>1.23</td>
<td>25</td>
<td>2.8</td>
</tr>
<tr>
<td>0.50</td>
<td>0.010</td>
<td>0.006</td>
<td>β + α′ + ω</td>
<td>72.0</td>
<td>995</td>
<td>1.38</td>
<td>18</td>
<td>3.0</td>
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<tr>
<td>0.09</td>
<td>0.13</td>
<td>0.005</td>
<td>β + α′ + ω</td>
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<td>720</td>
<td>1.13</td>
<td>33</td>
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<td>0.13</td>
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<td>β + α + α′ + ω</td>
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<td>990</td>
<td>1.51</td>
<td>12</td>
<td>2.9</td>
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<td>0.006</td>
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<td>910</td>
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<td>5.2</td>
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<td>0.42</td>
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<td>0.006</td>
<td>β + α + α′ + ω</td>
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<td>1045</td>
<td>1.47</td>
<td>2.1</td>
<td>3.1</td>
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<tr>
<td>0.39</td>
<td>0.51</td>
<td>0.005</td>
<td>β + α + α′ + ω</td>
<td>69.9</td>
<td>1190</td>
<td>1.70</td>
<td>1.7</td>
<td>3.1</td>
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</table>

E, dynamic Young’s modulus; σu, ultimate tensile strength; δ, plastic elongation; Hv, Vickers hardness.
oxygen is a β stabilizer in the investigated alloys with respect to the formation of both the α′ martensite and the ω phase, while its stabilizing effect for the α phase is not obvious. The effect of nitrogen in β-type titanium alloys appears complicated: it depresses both the α′ martensite and the ω phase on one hand, but promotes the formation of the α phase on the other hand.

Mechanical properties of the annealed alloys are also given in Table 1. It is clear that the increase of interstitial contents causes slight increase in dynamic Young's modulus; both tensile strength and Vickers hardness increase significantly but the ductility decreases sharply. Since nitrogen impairs ductility more significantly than oxygen, it is not as good a β strengthen as oxygen. Similar to Ti2448 alloy [11], annealing treatment results in an increase of Young's modulus of 4–8 GPa over the as-forged alloys.

The deformation curves of some of the investigated alloys are shown in Figure 3 and it can be seen that all alloys exhibit nonlinear elasticity. In particular, alloys with notable characteristics of “double yielding” (noted by arrows on the stress–displacement curves) due to the stress-induced MT [5] also undergo nonlinear elastic deformation prior to the MT. The stress–strain curves shown in Fig. 3b, d and f suggest that the increase of both oxygen and nitrogen results in more pronounced nonlinear elasticity (compare the two curves in Fig. 3f) and higher stress limit of elastic deformation, whereas the stress-induced MT impairs it. Phenomenologically, the effects of oxygen and nitrogen additions to Ti–30Nb–12Zr on the elastic stress limit are similar to grain refinement by warm rolling the M-Ti2448 alloy [17,18], because both measures depress the stress-induced MT. In essence, the elastic stress limit is raised in nonlinear elastic titanium alloys by improving the stability of the β phase through either composition design or grain refinement. Such alloying effects are also apparent from the ratios of tensile strength to dynamical Young’s modulus.
modulus as given in Table 1, and from the ratio of fatigue strength to yielding strength presented in Ref. [12].

Similar to other β-type titanium alloys, the investigated alloys exhibit small work-hardening rates as can be seen from Figure 3. It is also observed from the stress–displacement curves in Fig. 3a and c that with increasing levels of oxygen and nitrogen addition, the work-hardening rate decreases progressively. From the classical constitutive laws for plasticity as described by the Considéré criterion, the lack of hardening would induce localized plastic deformations (plastic instability) [20]. As a result, a drop in the plastic elongation is expected, and this is indeed the case (Table 1). The strengthening mechanism at the elastic deformation stage, however, may be different for different alloys. In the M-Ti2448, for example, homogeneous nucleation of dislocation loops was observed and, since this process is reversible, acted to raise the elastic stress limit. In the present alloys, the specific mechanisms of strengthening are not yet known, but they are certainly related to the additions of both O and N.

In summary, the nonlinear elasticity of β-type titanium alloys bears no intrinsic relationship to the \( e/a \) ratio. The initial phase constitution has a weak relation with such peculiar elastic deformation behaviour if the β phase is dominant, as evidenced by Gum Metal with \( (β + α) \) microstructure, Ti2448 alloy with single β and \( (β + α') + α \) microstructures and the studied alloys with \( (β + α' + α) \) and \( (β + α + α' + α) \) microstructures. Such elastic deformation behaviour would be neglected in many previous studies, probably because this non-linear characteristic was too weak in most alloys.

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