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Controlling reversible martensitic transformation in titanium alloys with high strength and low elastic modulus

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This paper reports on β-type titanium alloys with high β transus temperature and low martensite start temperature that display high strength and low elastic modulus. The strategy is based on Zr and Sn additions to Ti–Nb-based alloys. The α″ martensite in Ti–24Nb–4Zr–8Sn alloy is structurally much closer to the β phase than other alloys in terms of transformation strain and tetragonality, allowing homogeneously nucleated reversible mechanisms to be triggered before the formation of nanoscaled equiaxed α″ martensite by strain glass transition.

Keywords: Martensitic transformation; Titanium alloys; Elastic behavior; Strength; Lattice parameter

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Reversible martensitic transformation (MT) between the β phase, which has a body-centered cubic (bcc) structure, and the orthorhombic α″ martensite has recently attracted great attention due to developments of shape memory Ti alloys and multifunctional Ti alloys with high strength and low elastic modulus [1–6]. Among this last family of Ti alloys, Gum metals and Ti2448 alloy (with respective chemical compositions (in wt.%) of Ti–36Nb–2Ta–3Zr–0.3O [3] and Ti–24Nb–4Zr–8Sn [4]) have been shown to display peculiar nonlinear elasticity. In classical cases, this behavior can usually be related to a reversible stress-induced MT. However, as a softening mechanism [7,8], the reversible MT fails to explain the high ratio of strength to elastic modulus (approaching ~2%) of these alloys [3,4], similar in value to bulk metallic glasses with amorphous structure [9]. Besides the above controversial issues, some interesting features concerning the MT in these groups of alloys have been reported recently and are summarized as follows.

Firstly, a reversible transformation leading to nanosized α″ martensite with equiaxed morphology has been observed by an in situ tensile transmission electron microscopy (TEM) analysis of a modified Ti2448 alloy with low Sn and O contents (Ti–24Nb–4Zr–7.5Sn–0.08O) [10]. This martensite morphology is in sharp contrast with that resulting from conventional MT (displaying acicular morphology) but similar in shape to the stress-induced strain glass transition observed in non-martensitic NiTi alloys [11–13]. Additionally, the differential scanning calorimetry measurements fail to detect phase transformation peaks for both Ti2448 alloy and non-martensitic NiTi alloys [11,14]. This may suggest that the stress-induced strain glass mechanism could be a possible deformation mechanism for multifunctional Ti alloys, resulting in both high strength and low elastic modulus.

Secondly, the significant peak broadening of the stress-induced α″ martensite has been observed during a number of in situ X-ray diffraction (XRD) experiments on Ti2448 [15,16]. Synchrotron XRD measurements showed that the α″ martensite diffraction peaks were strong and sharp in a modified Ti2448 alloy in which the stress-induced MT has been proven to occur, but very weak and broadened in Ti2448 alloy [15]. Together with significant peak shifting of both β phase and α″ phases, the peak separation of the two phases is very difficult to detect, resulting in large errors. Since nanosized α″ martensite was observed during in situ TEM analysis [10], this peak broadening may be explained by the size effect. The calculation results suggested that the α″ martensite displays an average size of about ~2.5 nm [15]. Such a phenomenon was also

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observed in a Ti–Nb binary alloy containing a large amount of interstitial elemental O and explained by a nanosized lattice modulation resulting from the random distribution of O atoms [16].

Lastly, the occurrence of the stress-induced MT is strongly orientation dependent if measured on single orientated crystals. Tensile tests on single-crystal Gum metal showed that both $\langle 1\,0\,0\rangle$ and $\langle 1\,1\,1\rangle$ crystals exhibit a classical linear elastic deformation behavior, whereas the $\langle 1\,1\,0\rangle$ crystal clearly displays a pseudoelastic behavior with reversible strain up to 2.5% [17]. Subsequent analyses provided a reasonable explanation by demonstrating that the critical stresses to induce the MT, when loading along the $\langle 1\,0\,0\rangle$ and $\langle 1\,1\,1\rangle$ axes, were beyond the tensile strength [18]. Tensile tests on Ti2448 alloy showed similar deformation behavior, exhibiting a lower elastic modulus combined with higher strength and larger reversible strain when compared to Gum metals [19]. The critical stresses to trigger the MT have been estimated based on the assumption of pure shear stress for both $\langle 1\,0\,0\rangle$ and $\langle 1\,1\,1\rangle$ loaded crystals in both tensile and compression conditions and have been evaluated as lower than the corresponding tensile and compressive strength. However, no link could be established between the pseudoelasticity and the reversible MT for Ti2448. A possible mechanism of crystal distortion was then proposed to explain this peculiar behavior [19].

The above overview suggests that the nature of the MT in these β -type Ti alloys and its relation to the elastic deformation behavior are far from clear. Since both Gum metal and Ti2448 are Ti–Nb–Zr-based quaternary alloys, it might be meaningful to investigate the binary and ternary systems and to carry out a systematic analysis of the published data. In this work, it is shown that Ti–Nb-based Ti alloys with single β phase having both higher phase transformation (T_β) temperature from the β phase to the α phase and lower M_s temperature to the α'' martensite generally display lower elastic modulus. This means that the β phase should ideally have low chemical stability with respect to α phase precipitation but high chemical stability with respect to α'' martensite precipitation. This fact validates the combined addition of neutral elements Zr and Sn as a way to maximize the ΔT (T_β–M_s) range. It will also be shown that the α'' martensite in Ti2448 alloy is structurally much closer to the β phase than other Ti alloys in terms of tetragonality and transformation strain.

Variations of the Young's modulus at room temperature with Nb content in binary Ti–Nb, ternary Ti–Nb–(8,10,12)–Zr and quaternary Ti–Nb–4Zr–7.5Sn systems are plotted in Figure 1a. The figure shows clearly that the minimum value of the modulus decreases from the binary system to the ternary and quaternary systems, while the corresponding Nb content at the modulus valleys shifts from ~40% to ~32% and ~24%. The alloys outside of the region bounded by the parallel lines in Figure 1a contain ω phase with higher modulus than the β phase and can be ignored for the present purpose. The T_β temperatures of the alloys within the bounding region are estimated using an empirical method [21]: $T_\beta = 1158 - 8.5[\mathrm{Nb}] - 2[\mathrm{Zr}] - 0[\mathrm{Sn}] + 200[\mathrm{O}]$, in which the element in square brackets describes its wt.% concentration in the alloy. The plot of elastic modulus vs. T_β in

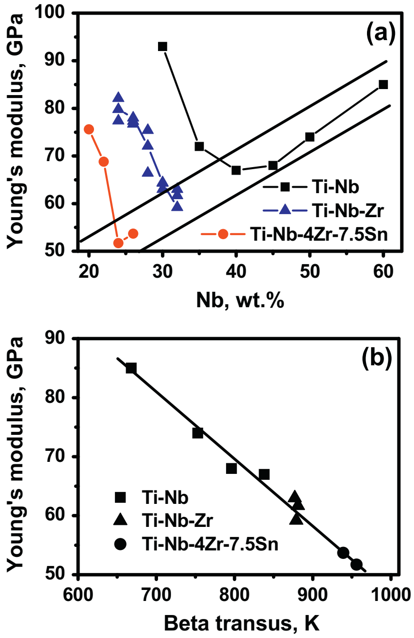

Figure 1. Variations of Young's moduli with Nb content (a) and β transus (b) of Ti–Nb [7], Ti–Nb–(8,10,12)Zr [20] and Ti–Nb–4Zr–7.5Sn [14] alloys; the alloys within the region bounded by the parallel lines in (a) contain almost single β phase and the plot in (b) contains only data for these alloys.

Figure 1b shows clearly a linear relationship for the alloys containing single β phase or β plus a small volume fraction of ω phase.

The data in Figure 1b suggest that a low elastic modulus can be achieved by retaining the high-temperature β phase at room temperature. Since these alloys typically have T_β temperatures ranging from 850 to 1000 K, retention of β phase at room temperature necessarily creates a high level of metastability, and stress-induced phase transformations such as α'' martensite and/or ω phase formation are likely to occur upon loading. From an applicative point of view, the key point is the critical stresses required to induce these transformations and the influence of the transformations on the macroscopic deformation behavior and mechanical properties. Recent studies have highlighted that the elastic softening due to the reversible MT in β -type Ti alloys may cause detrimental effects on the stress- and strain-controlled fatigue properties [22–24]. The suppression of the MT or, at least, a delay in reaching the higher critical stress is therefore crucial regarding the potential load-bearing applications of these alloys.

It should be noted that the data in Figure 1 were taken from alloys annealed at high temperatures in single β phase field in order to avoid the effect of texture. The T_β temperatures of Ti–35Nb–7Zr–5Ta, Ti–29Nb–13Ta–4.6Zr and Ti–36Nb–2Ta–3Zr–0.3O (Gum metal) estimated using the empirical method are in the range 860–900 K. The corresponding elastic moduli estimated from the relation shown in Figure 1b are ~60 GPa, in rough agreement with experimental data [25,26]. This suggests that the relationship of elastic modulus vs. T_β established from the Ti–Nb–Zr–Sn system can be used to estimate the elastic modulus of other alloys. It should be pointed out that the condition for the application of