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Comparative study of structure formation and mechanical behavior of age-hardened Ti–Nb–Zr and Ti–Nb–Ta shape memory alloys

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ABSTRACT

This work sets out to study the peculiar effects of aging treatment on the structure and mechanical behavior of cold-rolled and annealed biomedical Ti–21.8Nb–6.0Zr (TNZ) and Ti–19.7Nb–5.8Ta (TNT) (at.%) shape memory alloys by means of transmission electron microscopy, X-ray diffractometry, functional fatigue and thermomechanical testing techniques. Dissimilar effects of aging treatment on the mechanical behavior of Zr- and Ta-doped alloys are explained by the differences in the ω-phase formation rate, precipitate size, fraction and distribution, and by their effect on the alloys' critical stresses and transformation temperatures. Even short-time aging of the TNZ alloy leads to its drastic embrittlement caused by "overaging". On the contrary, during aging of the TNT alloy, formation of finely dispersed ω-phase precipitates is gradual and controllable, which makes it possible to finely adjust the TNT alloy functional properties using precipitation hardening mechanisms. To create in this alloy nanosubgrained dislocation substructure containing highly-dispersed coherent nanosized ω-phase precipitates, the following optimum thermomechanical treatment is recommended: cold rolling (true strain 0.37), followed by post-deformation annealing (600 °C, 15–30 min) and age-hardening (300 °C, 30 min) thermal treatments. It is shown that in TNT alloy, pre-transition diffraction effects (diffuse reflections) can "mask" the β-phase substructure and morphology of secondary phases.

1. Introduction

Zirconium- and tantalum-doped nickel-free Ti–Nb-based shape memory alloys (SMAs) are among the most promising metallic materials for medical implants. They contain exclusively biocompatible components, thus providing high corrosion resistance and biochemical compatibility [1–5], whereas their superelastic behavior and low Young's modulus are close to those of bone tissues [6–9]. The structure and functional properties of these alloys depend on a complex sequence of phase transformations, including reversible $\beta \leftrightarrow \alpha''$ and $\beta \leftrightarrow \omega$ transformations, and can effectively be controlled by a technological sequence comprising plastic deformation, post-deformation annealing (PDA) and age-hardening heat treatments [7,10–12].

Zirconium belongs to the same IVa group of the Periodical System as titanium, while tantalum belongs to the same Va group as niobium. Since they are analogous to different elements of a basic Ti–Nb alloy, the addition of zirconium to the binary Ti–Nb composition can be considered as an enrichment of the titanium side, while the addition of tantalum, as an enrichment of the niobium side. Zr and Ta thereby bring their specific features to the physical nature of the basic binary alloy, with different effects on the structural and phase transformations triggered by thermomechanical treatment (TMT) in each of the ternary Ti–Nb–Zr and Ti–Nb–Ta alloys. One such essential dissimilarity is a different tendency to ω-phase formation: the introduction of zirconium in Ti–Nb SMA promotes ω-phase formation, while the introduction of tantalum suppresses it [13,14].

Generally speaking, ω-phase is observed in Ti-based and Zr-based alloys either after rapid cooling of these alloys to retain the high-temperature BCC β-phase at a low temperature ("athermal" ω-phase), or after the aging of these alloys in a certain intermediate temperature range ("isothermal" ω-phase) [13,15,16]. The omega-phase is especially interesting, first, because it increases the strength of Ti-based alloys as a result of dispersion hardening (admittedly at a cost of less ductility), and, second, because it improves the superconducting properties of titanium and zirconium alloys [13,16].

The following positive effects ω-phase dispersion hardening plays in the realization of the superelastic behavior in binary Ti–Nb alloys were described: the greater difference between the "dislocation" and the "transformation" yield stresses and the lower propensity to stabilization of α''-martensite during superelastic cycling [7,10,17,18]. As a result, superelastic recovery strain increases, while residual strain and mechanical hysteresis decrease. It was also shown that a specific combination of highly dispersed ω-phase particles with submicro-grained/

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Table 1
TNZ and TNT ingot compositions in at.(wt.)% and characteristic temperatures.

	Ti	Nb	Zr	Ta	O	C	N	H	T_m,°C	M_f; M_s; A_s; A_f, °C
TNZ	71.2 (57.1)	21.8 (33.9)	6.0 (9.0)		--- (0.13)	--- (0.01)	--- (0.01)	--- (0.007)	1775	<-150;-62;-101;-45
TNT	74.5 (55.4)	19.7 (28.4)		5.8 (16.2)	--- (0.047)	--- (0.009)	--- (0.010)	--- (0.006)	1930	<-150;+20;-84;+160

T_m were evaluated using data from [21] for Ti-Nb-Zr and from [22] for Ti-Nb-Ta.
M_s, A_s, A_f were evaluated in as-received state using a *DIL805A/D* dilatometer.

subgrained β-phase structure represents the most beneficial microstructure for Ti–Nb alloys' superelasticity [18].

In comparing the Ta- and Zr-doped Ti–Nb SMA, it was shown that on one hand, age-hardening of the TMT-processed nanosubgrained Ti–19.7Nb–5.8Ta alloy (TNT) increased the alloy's superelastic fatigue life and decreased the residual strain accumulated during cycling [14]. On the other hand, even a short-term aging (~15 min) of the TMT-processed Ti–22Nb–6Zr alloy (TNZ) severely deteriorated the alloy's functional characteristics [19,20]. This deterioration was explained as a direct result of rapid precipitation growth and a loss of coherency of the preexisting nanosized ω-phase particles.

To bring about a better understanding of the omega-phase formation dissimilarities between the TNZ and TNT alloys, this work presents a comparative study of the influence of thermomechanical processing on their structure and on their mechanical static and dynamic (fatigue) properties. The TMT comprised of moderate cold rolling (CR), post-deformation annealing (PDA) and aging heat treatment (AG). The alloy samples were characterized by single- and multi-cycle isothermal tensile testing and constant-strain temperature scanning (recovery stress generation) techniques. Transmission electron microscopy (TEM) and X-ray diffractometry (XRD) techniques were used for the comparative structure analysis in the quest for explanations of the observed differences in the functional

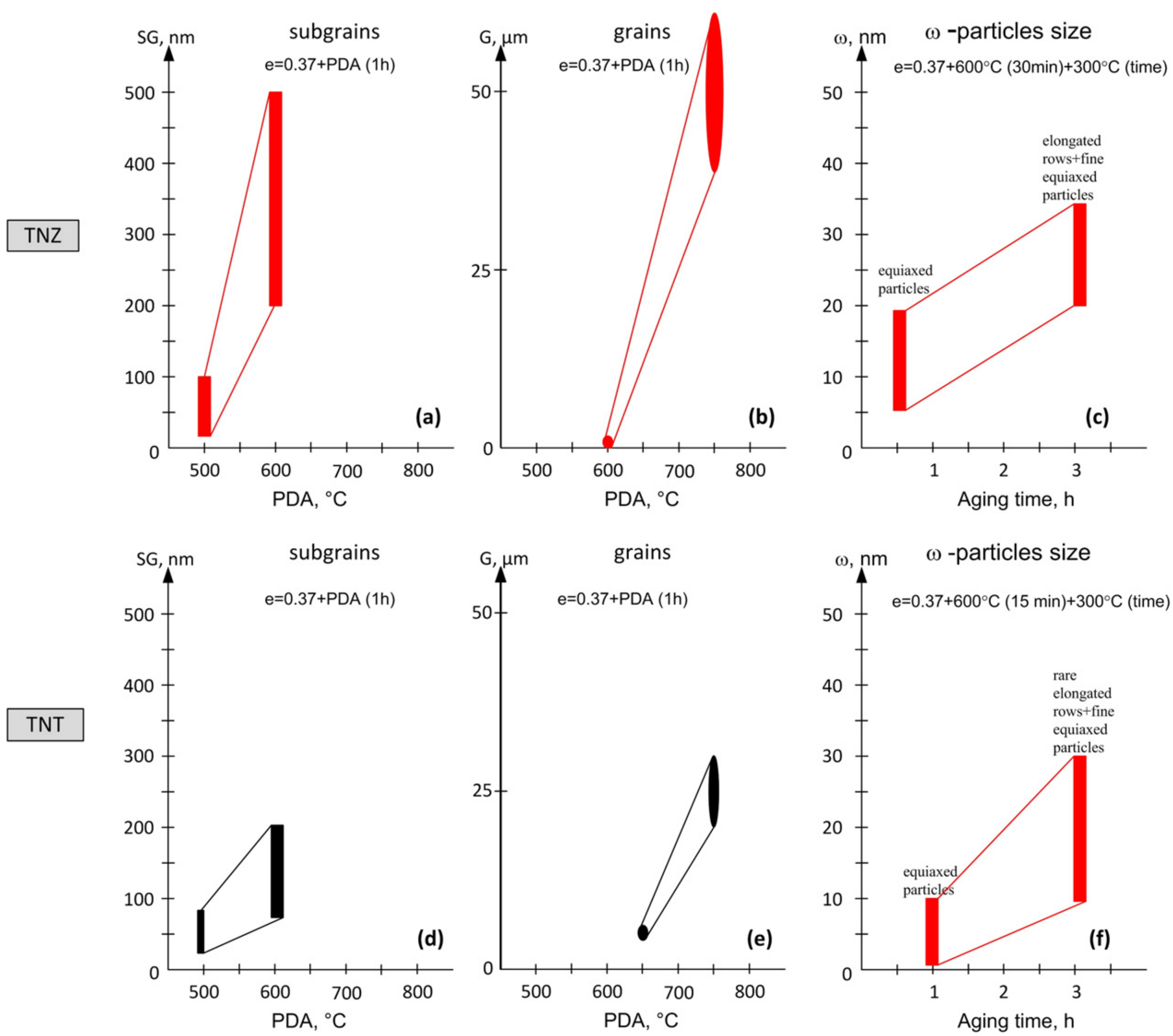

Fig. 1. Beta-phase subgrain and recrystallized grain sizes as functions of the post-deformation annealing temperature and omega-phase particle size as a function of the age-hardening time at 300 °C for TNZ (a, b, c) and TNT (d, e, f).
Data are collected from this work and also from [14,19,24].