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Microstructural evolution in a superelastic metastable beta-Ti alloy

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ABSTRACT

The microstructural evolution of Ti-24Nb-4Zr-8Sn wt.% during low-temperature ageing is examined by atom-probe tomography (APT) and X-ray diffraction (XRD). This ageing is deleterious to the desirable mechanical properties, such as ultra-low elastic modulus and superelasticity. Initially, the cold-rolled alloy possesses a martensitic α''-precipitate/β-matrix microstructure. On ageing, Ti-rich/solute-lean precipitates grow in linear arrangements, which are likely associated with dislocations. Additionally, the composition and number density of Nb-rich domains (which are associated with superelasticity) are quantified for the first time. The domains are unstable, but decrease in number density during ageing, causing the deterioration in mechanical properties.

Ti-24Nb-4Zr-8Sn wt.% (Ti-15Nb-3Zr-4Sn at.%), commonly referred to as Ti-2448, is a Gum-like [1] metastable β-Ti alloy being developed for biomedical applications. In its thermodynamically stable state this alloy consists of body-centered cubic (bcc) β and hexagonal closed-packed (hcp) α phases. However, on quenching from above the β-transus temperature, the β-structure is almost fully retained to room temperature along with strain-induced phases, such as α'', δ, and athermal ω [2–6]. Quenched Ti-2448 possesses a non-linear elastic response with an ultra-low elastic modulus and a hysteresis loop on loading-unloading (corresponding to energy absorption) [7] due to a stress-induced phase transformation [2].

To develop β-Ti alloys further and broaden their range of applications, it is necessary to relate instabilities in mechanical properties to mechanically and thermally induced microstructural evolution. In the present work atom-probe tomography (APT) and laboratory X-ray diffraction (XRD) were used to study Ti-2448 following cold-rolling samples and ageing at 300 °C for 4 h and 8 h, respectively. XRD shows that the alloy initially possesses a martensitic-α'' precipitate/β-matrix microstructure. On ageing, Ti-rich/solute-lean nanoprecipitates nucleate and form linear arrangements, which are likely associated with dislocations. These may be ω and/or α phase, which is difficult to distinguish in this case as metastable ω is a precursor to nanoscale α-formation [8]. Number density and composition of metastable Ti-lean, Nb-rich precipitates are quantified for the first time, and the number density decreases with ageing time. This is significant, as Nb-rich domains are the source of the desirable non-linear elastic properties [2], thus the cause of deterioration of the elastic properties with low temperature ageing [7] is now identified.

A plate of Ti-2448 was supplied from the Chinese Academy of Science Institute of Metal Research, Shenyang National Laboratory for Materials Science. The plate had been cold-rolled to 90% strain. Two samples were then heat-treated at (i) 300 °C/4 h and (ii) 300 °C/8 h, followed by air-cooling. Needle-shaped APT samples of the heat-treated conditions were prepared using a standard lift-out method utilising a FEI Helios NanoLab 600 DualBeam focused ion-beam (FIB) microscope equipped with an Omniprobe micromanipulator. A detailed description of the FIB lift-out and tip sharpening procedure can be found in references [9–11].

Laboratory XRD measurements were performed on the Ti-2448 plate following cold-rolling, and the 300 °C/4 h and 300 °C/8 h heat-treatments. XRD was performed on a Rigaku Ultima IV using Cu-K $_{\alpha}$

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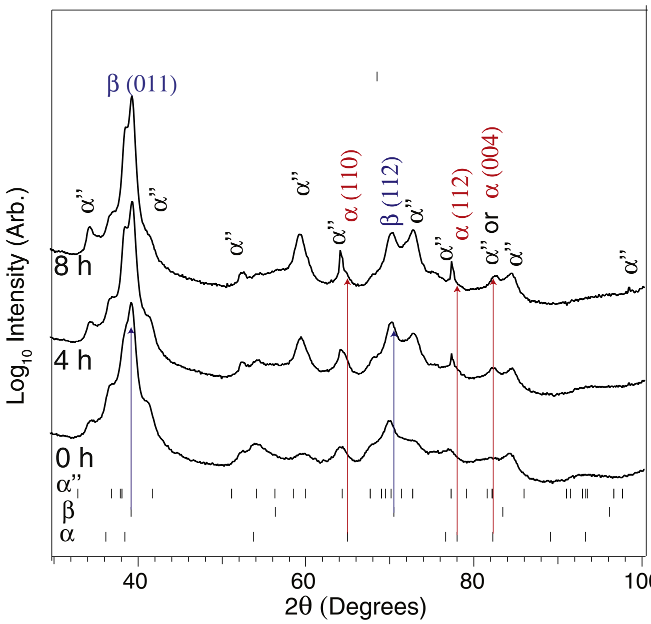

Fig. 1. Laboratory XRD profiles for Ti-2448 in the initial cold-rolled condition, and after 300 °C/4 h and 300 °C/8 h ageing.

X-ray radiation with a characteristic wavelength of 1.541 Å at 40 kV and 20 mA. Data were collected over a range of 30–100° 2θ. Phase identification was performed using the program CrystalDiffract.

APT experiments were performed in the laser mode using a Cameca LEAP 4000X Si equipped with a 355 nm UV picosecond laser at the Northwestern University NUCAPT core facility. The specimen stage temperature was 30 K and pulse energies of 20 pJ were used. Data reconstruction and analysis was performed using IVAS.

The X-ray diffraction patterns of cold-rolled and aged Ti-2448 samples are shown in Fig. 1. It is clear that the initial processing with cold-rolling has induced extensive α'' phase. The α'' peak positions were determined from Liu et al. [2]. Almost all the peaks of the other potential phases lie very close to α''-reflections, so it is difficult to determine if other phases are contributing to the diffraction spectra. The highlighted peaks at 64.0°, 75.2° and 77.2° indicate that another phase *may* be present. These peaks grow in intensity and appear to correspond to α-reflections. Liu et al. [2] commented that compressive plastic strain (such as cold-rolling) induces ω formation in this alloy. Indeed, ω has been previously identified in Ti-2448 by TEM, following cold-rolling and also following low temperature ageing, despite not being observed by laboratory XRD [7].

The bulk needle compositions determined from APT are in good agreement with bulk compositions measured by ICP-OES and LECO analyses, Table 1. Inspection of the concentration frequency distribution functions shows that the experimental data for Ti and Nb are broader than the binomial function, indicative of the presence of Ti-rich, Nb-lean regions and Ti-lean, Nb-rich regions, Fig. 2.

Ti and Nb isoconcentration surfaces were drawn with concentration values equaling the average of the far-field concentrations in the matrix and the concentrations in the precipitate core. The APT reconstructions of the 4 h and 8 h heat-treated sample are shown in Fig. 3. The Ti-rich phase is highlighted in blue, and the Nb-rich

Table 1
Nominal composition of Ti-2448 in at.% and composition measured by inductively coupled plasma optical emission spectrometry (ICP-OES) and LECO gas analyses. The compositions measured by APT and the total number of million atoms used in the reconstructions of each APT measurement are listed.

	Ti	Nb	Zr	Sn	O	Atoms (M)
Nominal composition	78.3	15.1	2.6	3.9	–	–
ICP-OES	80.4	13.3	2.5	3.5	0.3	–
APT 4 h	79.0	13.7	2.9	3.7	0.4	11
APT 8 h	80.0	12.7	2.8	3.8	0.3	28

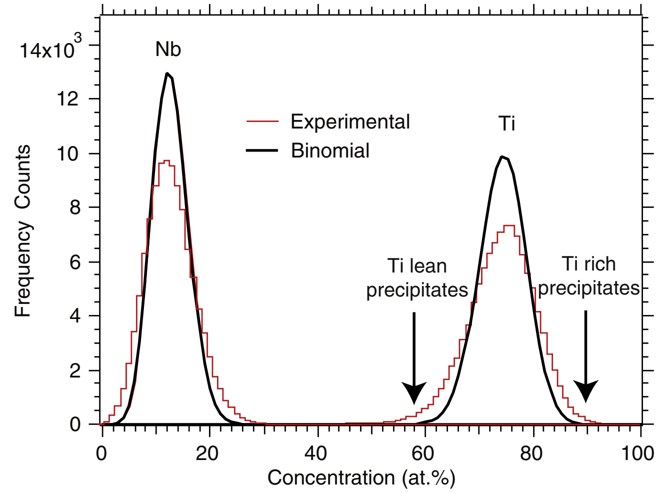

Fig. 2. Ti and Nb concentration frequency distributions constructed with a block size of 100 atoms, for Ti-2448 with a 300 °C/4 h heat-treatment. The binomial distribution is shown for comparison.

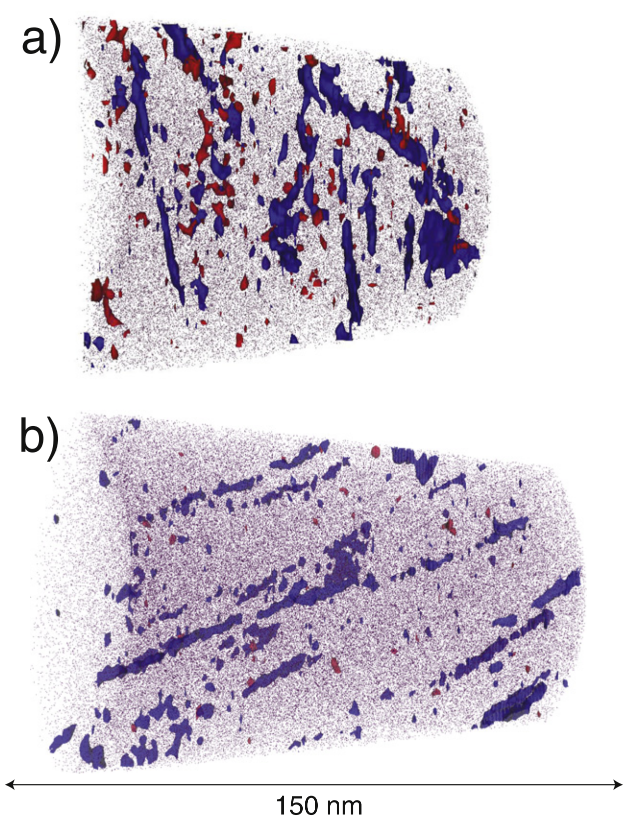

Fig. 3. APT reconstructions of a Ti 85.5 at.% isoconcentration surface (blue) and Nb 22.8 at.% isoconcentration surface (red) for a) Ti-2448 + 300 °C/4 h, and b) Ti-2448 + 300 °C/8 h, with 25% of the Zr atoms displayed (purple). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)