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.

Key words: atom-probe tomography, martensitic phase transformation, precipitation, titanium alloys, ageing

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 composi-

tion 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 α 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 ° 2 θ . 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.

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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

The X-ray diffraction patterns of cold-rolled and aged Ti-2448 samples are shown in Figure 1. It is clear 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 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, Figure 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 Figure 3. The Ti-rich phase is highlighted in blue, and the Nb-rich phase is highlighted in red. The Ti-rich precipitates appear to be in linear arrangements, presumably along dislocation lines given the extent of cold-rolling deformation the material had been subjected to. The Ti-rich precipitates appear in two size groups: (i) very fine nanoscale precipitates typical of ω ; and (ii) larger lath structures typical of α . The Nb-rich nanoscale precipitates are more uniformly dispersed throughout the needles. As the needle is predominantly the bcc- β phase, an estimate of the precipitate number density can be obtained from knowledge of the pure β -Ti unit cell volume [12] and the total number of atoms counted. The number density of the Nb-rich precipitates in each measurement was approximately $1.2 \times 10^{23} \text{ m}^{-3}$ after 4 h heat-treatment, and decreased by an order of magnitude to $0.1 \times 10^{23} \text{ m}^{-3}$ after 8 h heat-treatment, for the stated Nb isoconcentration surface values.

The isoconcentration surfaces employed enabled generation of proximity histogram concentration profiles (prox-

Figure 1: Laboratory XRD profiles for Ti-2448 in the initial cold-rolled condition, and after $300^\circ\text{C}/4\text{h}$ and $300^\circ\text{C}/8\text{h}$ ageing.

grams) [14–19], to examine, in detail, the composition of each phase after each heat-treatment, Figure 4. The Ti-rich precipitates were depleted in Nb, Zr, and Sn solute additions. In a previous study, the authors identified ω -precipitates in Ti-5Al-5V-5Mo-3Cr wt.% (Ti-5553) as Ti-rich, solute-depleted precipitates [13]. In the case of Ti-5553 the morphology and size seen by APT were concomitant with that of a dispersed ω -phase. Similarly to Ti-5553 [13], in Ti-2448 APT results it was observed that the Ti-rich precipitates occurred as very fine nanoscale precipitates that are associated with ω , but had also formed a lath-like structure that is typical of the α -phase. It is well known that the ω -phase is a metastable precursor phase that forms upon low-temperature heat-treatments prior to the formation of the stable α -phase [6, 8]. Thus, in this case we conclude that the Ti-rich precipitates observed were a combination of fine ω -discs and α -laths, of similar Ti-rich, solute-lean composition but with different crystal structures. This is reasonable, as ω and α have previously been identified by TEM under similar ageing conditions in Ti-2448 [7], and the diffraction peaks associated with α grow in intensity with heat-treatment time in the XRD data, Figure 1. On the matrix-side of the interface, Figure 4, there is a clear Ti depletion zone compared to the far-field composition, and a corresponding Nb, Sn, and Zr enrichment-zone. Oxygen segregation is observed as an increase of O concentration in the interfacial region, similar to what has been observed in Ti-5553 [13].

It is difficult to assign a crystal structure to the Ti-lean, Nb-rich precipitates based on the proxigram compositions alone. However, based on the XRD data it is reasonable to associate this phase with α'' , Figure 1. In this case, the number density decreases between the 4 h and 8 h thermal exposures, concomitant with martensitic phases being removed on annealing [20]. Unlike the Ti-rich precipitate formation, there is no segregation of O at the interface of

Figure 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.

the Nb-rich precipitates, Figure 4. Sn and Zr were slightly depleted in the Ti-lean α'' -precipitates, and it was predominantly a direct substitution of Nb for Ti. The Ti was depleted by about ~ 20 at.% within the precipitates, compared to the far-field concentrations, and the precipitates were enriched by this amount with Nb, compared to the far field concentrations. The quenched and low-temperature aged Ti-5553 material alloy did not contain the Ti depleted α'' -phase when analysed by APT [13].

Previously it was observed that low-temperature heat-treatment of Ti-2448 was detrimental to the non-linear elastic properties on loading, and this was attributed to the formation of the ω -phase by TEM analysis [7]. However, Liu *et al.* [2] identified nanoscale α'' precipitates that they refer to as embryos, which grow in size on loading, contributing to a non-linear, low-stiffness elastic regime. There is a decrease in number density of the Ti-lean, Nb-rich phase that may be α'' embryos, and this would contribute to the previously observed removal of the non-linear elastic regime when annealed [7].

Mo and V are also frequently used to stabilise the β -phase to room temperature [20]. Low temperature ageing increases the stiffness of Ti-V and Ti-Mo binary alloys [21, 22], and was previously associated with precipitation of the ω and α phases. To the authors' knowledge, the presence of solute rich α'' embryos has not been examined in detail for Ti-V and Ti-Mo, and we can only hypothesise that the observations herein are applicable to those alloys.

In summary, the alloy initially possesses α'' martensite within a β -matrix, induced from the cold-rolling process. Following ageing at 300 °C, (i) Ti-rich/solute-depleted ω and α -precipitates form in linear arrangements that likely are associated with dislocations, and (ii) A Ti-lean/Nb-enriched phase is also identified. The Nb-enriched domains are unstable, and decrease in number density with ageing time. This is of significance, as the Nb-rich domains are the source of the desirable non-linear elastic properties [2]. The dissolution of the Nb-rich domains at 300 °C (representative of low-temperature ageing) is identified as the cause of deterioration of the elastic properties [7] for the first time. (iii) O partitions to the interface of the Ti-rich phase, and this has been previously noted to occur in Ti-5553. This partitioning is not observed at the Ti-lean/Nb-rich precipitate interface with the matrix.

Figure 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).

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Figure 4: (1a - d) Proximity histogram concentration profiles of Ti-2448 in the 300 °C/4 h and 300 °C/8 h heat-treated conditions averaged over identified precipitates using a LEAP 4000X Si, for the Ti 85.0 at.% isoconcentration surface (4 h sample) and Ti 85.5 at.% isoconcentration surface (8 h sample). (2a - d) Proximity histogram concentration profiles of the same samples for the Nb 23 at.% isoconcentration surface (4 h sample) and Nb 22.8 at.% isoconcentration surface (8 h sample). The inflection point for the 8 h Ti isoconcentration surface data is highlighted with a dashed line (1a - d), and the Nb isoconcentration surface data (2a - d) as an approximation for the center of the interfacial region between the β matrix and the precipitates (ppt).

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