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Characterizing nanoscale precipitation in a titanium alloy by laser-assisted atom probe tomography

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ABSTRACT

Atom-probe tomography was performed on the metastable β-Ti alloy, Ti-5Al-5Mo-5V-3Cr wt% (Ti-5553), aged at 300 °C for 0 to 8 h, to precipitate the embrittling isothermal ω phase. Accurate precipitate quantification requires monitoring and controlling suitable charge-state ratios in the mass spectrum, which in turn are closely related to the laser pulse energy used. High ultraviolet laser pulse energies result in significant complex molecular ion formation during field-evaporation, causing mass spectral peak overlaps that inherently complicate data analyses. Observations and accurate quantification of the ω-phase under such conditions are difficult. The effect is minimized or eliminated by using smaller laser pulse energies. With a small laser pulse energy, Ti-rich and solute depleted precipitates of the isothermal ω phase with an oxygen enriched interface are observed as early as after 1 h aging time utilizing the LEAP 5000X S (77% detection efficiency). We note that these precipitates were not detected below a 2 h aging time with the LEAP 4000X Si (58% detection efficiency). The results are compared to the archival literature. The Al concentration in the matrix/precipitate interfacial region increases during aging. Nucleation of the α-phase at longer aging times may be facilitated by the O and Al enrichment at the matrix/precipitate interface (both strong α-stabilisers). The kinetics and compositional trajectory of the ω-phase with aging time are quantified, facilitating direct correlation of the APT data to previously published mechanical testing.

1. Introduction

Near α-Ti alloys, α plus β-Ti alloys and metastable β-Ti alloys are susceptible to thermally induced phase-transformations, which dramatically alter their mechanical properties. The characterization and quantification of these phases can be inherently difficult, particularly when the precipitates are small (< 10 nm) relative to the thickness of a TEM foil or when the compositional contrast between the precipitate and matrix is small, making detection by atom-probe tomography (APT) challenging. Such limitations with characterization methods have hindered our understanding of α_2 formation in near-α and α plus β-Ti alloys, which is detrimental to fracture toughness and cold dwell fatigue resistance of components in gas-turbine engines [1–6]. It has also hindered our understanding of athermal ω (ω_a), which forms on quenching, and isothermal ω (ω_i), which forms on subsequent low-temperature aging of metastable β-Ti alloys [7–12]. The ω_a phase forms by a diffusionless transformation. The ω_i phase forms by subsequent diffusion during low-temperature aging at and below ~350 °C and therefore it possesses a different composition from that of the β-matrix. Typically, the ω-phase is undesirable as it embrittles the alloy [10]; it is, however, generally believed to be a precursor to the formation of stable nanoscale α-precipitates that highly strengthen the alloy [8,9,13,14]. This precipitation sequence is not fully understood, and a vast amount of APT research has been published recently to help further our insight into the precipitation mechanisms of the high-strength-to-weight β-Ti alloys: Ti-5Al-5Mo-5V-3Cr wt% (Ti-5553); and Ti-6Cr-5Mo-5V-4Al (wt%) (Ti-6554) [9,11–17].

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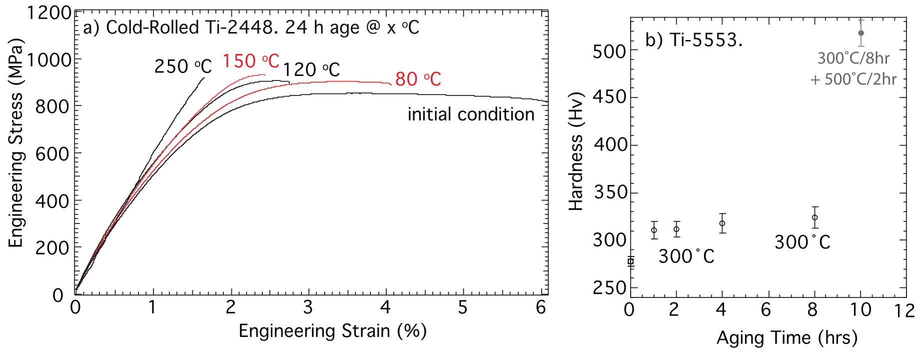

Fig. 1. a) Effect of low temperature aging between 80 and 250 °C for 24 h on room-temperature tensile properties of cold rolled metastable β-Ti alloy Ti-2448 (Ti-24Nb-4Zr-8Sn wt%) [10]. b) Effect of low temperature aging on room-temperature hardness of Ti-5553 (Ti-5Al-5Mo-5V-3Cr wt%). Samples were aged at 300 °C for up to 8 h, and a dual heat-treatment sample of 300 °C/8 h + 500 °C /2 h was also performed [9]. Images reproduced with the permission of the publisher.

Fig. 1(a) illustrates the deleterious effects on mechanical properties associated with ω_i precipitation in 24 h aged Ti-24Nb-4Zr-8Sn wt% (Ti-2448) [10]. The alloy became increasingly brittle and stiff with higher aging temperatures up to 250 °C. It is striking that an age of just 80 °C/24 h has such a profound effect on mechanical properties. Identifying such early stage precipitation of ω_i from ω_a by TEM is inherently complicated. The associated diffraction spots are weak and diffuse and diffraction spot brightness is dependent on foil-thickness. Such weak diffraction also complicates dark-field imaging. In the study of Ti-2448 the embrittlement following the 80 °C/24 h treatment could only be associated with ω_i formation from the trend in the mechanical data and observing ω_i formation in the 250 °C/24 h aged sample. Fig. 1(b) shows an increase in Vickers hardness of Ti-5553 after a 300 °C/1 h aging treatment, associated with ω_i formation [10]. Previously, these precipitates were not identified in this heat-treatment by APT analyses utilizing a LEAP 4000X Si [11] but were observed by TEM and small-angle neutron- scattering (SANS) [10]. This introduction highlights that advancement in materials characterization techniques is required to characterize the earliest stages of nanoprecipitation, which can alter dramatically the mechanical properties.

The ongoing development of commercially available local-electrode atom-probe (LEAP) tomographs has recently permitted unparalleled compositional analyses of nanoscale precipitates in Ti-alloys. Characterization of the ω-phase in Ti-5553 and Ti-6554 alloy has been attempted with voltage pulsing [13,18] and laser pulsing [9,11,14,15,17]. Because ω-phase containing Ti-alloys are brittle, laser pulsing can assist in achieving more data per APT experiment prior to specimen fracture. The laser pulse energy can induce undesirable thermal effects, such as surface diffusion or the formation of complex molecular ions. The thermal effects make data analyses more difficult and can obscure second phase precipitates, possibly influencing data regarding ω-phase found in the literature. There are clear differences in the results obtained regarding the ω-phase in β-Ti alloys, specifically focusing on Ti-5553 and Ti-6554. The first APT measurements of Ti-5553 with a 2 h aging treatment at 350 °C identified the ω-precipitates as a phase with very similar composition to that of the β- matrix [18]. More recently, the same authors demonstrated that slow heating at 5 °C/min to 350 °C (a 70 min aging treatment) resulted in ω-phase precipitates, which are depleted in all solute additions [13]. This is in agreement with our current observations. Finally, it has also recently been reported that the ω-phase in Ti-6554 aged at 300 °C for 0 to 8 h is a Mo-depleted precipitate, with all the other solute additions equal to their bulk concentrations [14,17]. Such results are of significance as they are used to rationalize the precipitation sequence of $\beta \rightarrow \beta + \omega_a \rightarrow \beta + \omega_i \rightarrow \beta + \alpha$. Thus, a study of the characterization of the ω-phase in β-Ti alloys by APT is timely and warranted.

This article demonstrates potential characterization errors, which can arise when the laser pulse energy is too high. It also notes a case where early stage precipitation is detected and characterized by the LEAP 5000X S and *not* the LEAP 4000X Si, which suggests that there may also be an instrumental dependence. Our results do not identify athermal ω-formation at Mo depleted zones in Ti-5553, in agreement with SANS measurements of the same alloy [9]. The titanium-rich and solute-depleted isothermal ω-phase is identified as early as after 1 h aging at 300 °C, in agreement with [13]. Finally, the evolution of the isothermal ω-phase between 0 and 8 h aged at 300 °C is quantified herein.

2. Materials and Methods

2.1. Sample Preparation

The forged billet of Ti-5553 used in this research has previously been studied and described [9,19]. All samples were prepared by initially heat-treating Ti-5553 at 900 °C for 30 min, followed by water quenching. Four samples were subsequently aged at 300 °C for 1, 2, 4, and 8 h and finally air-cooled. These aging conditions complement previously published studies of Ti-5553 by small-angle neutron-scattering (SANS), transmission electron microscopy (TEM), micro-hardness measurements and APT [9,11]. All heat-treatments were performed with the samples encapsulated within an argon atmosphere.

Following heat-treatment, APT samples of the quenched condition and aged conditions were prepared using a standard lift-out, nanotip mounting, and nanotip sharpening method [20] employing an FEI Helios NanoLab 600 Dual-Beam focused ion-beam (FIB) microscope equipped with an Omniprobe Autoprobe 200 micromanipulator. Additional aspects of the FIB lift-out procedure can be found elsewhere, for example [21].

2.2. APT Data Acquisition & Test Matrix

All APT experiments were performed with laser pulsing on Cameca's LEAP instruments, representing four different models and configurations at different research facilities. The full test matrix is displayed in Table 1, which was designed to examine the dependence of precipitate identification and quantification with laser pulse energy and with the relative intensities of the peaks for different charge states (the so-called *charge-state* ratios (CSR)).

The HR tomographs have an energy-compensating reflectron lens that improves mass resolution mostly in voltage mode and reduces background noise to some degree, albeit with decreased detection efficiency. The Si and S tomographs have a straight flight-path with higher detection efficiency. The detection efficiency of the reflectron instruments (LEAP 3000X HR and LEAP 4000X HR) is ~37%, while the LEAP 4000X Si and LEAP 5000 XS straight flight-path instruments have ~58 and ~77% detection efficiency, respectively [22,23]. The LEAP 3000X HR is equipped with a green laser, $\lambda = 532$ nm and is marked by an asterisk* in Table 1, while all other tomographs in this work are equipped with a UV picosecond laser, $\lambda = 355$ nm. The laser pulse energies and specimen stage temperatures used for each measurement are listed along with the specific tomograph, ion detection efficiency, total ion counts of each measurement run in millions (M) detected, and