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Alpha phase precipitation from phase-separated beta phase in a model Ti–Mo–Al alloy studied by direct coupling of transmission electron microscopy and atom probe tomography

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Nucleation and growth of alpha precipitates during low-temperature annealing of Ti–10 at.% Mo–10 at.% Al alloy was investigated using direct coupling of transmission electron microscopy and atom probe tomography. The initial stages of annealing at 400 °C showed structurally well-defined alpha precipitates that were depleted in Mo as well as Al, and were confined within the Ti-rich beta phase separated pockets. The Al-enriched alpha phase was only observed after further annealing at 600 °C.

Keywords: Three-dimensional atom probe (3DAP); Atom probe tomography; Phase transformations; Titanium alloys; Transmission electron microscopy (TEM)

Beta titanium alloys are increasingly being used in a wide range of applications from aerospace to biomedical applications [1–3]. In beta titanium alloys the morphology and distribution of alpha phase depends on the nucleation sites, like prior beta phase separation, the presence of metastable omega phase and beta phase grain boundaries. These multiple nucleation pathways can coexist and compete with each other depending upon the composition of the alloy and the nature of the heat treatment [4,5]. This makes it very difficult to investigate the fundamental mechanism of alpha phase nucleation in commercial multicomponent alloys. Thus model alloys are usually developed and various thermal treatments are designed so as to decouple these pathways and understand the influence of each nucleation site on alpha precipitation. In this study the focus was to investigate the role of prior beta phase separation on the nucleation of alpha phase in a model ternary Ti–10 at.% Mo–10 at.% Al (Ti–10Mo–10Al) alloy by long-term annealing of beta-solutionized and water-quenched samples. Mo and Al were chosen to be the preferred alloying additions as they form the basis of several commercial and model titanium alloys [4,5]. Also, as per the studies of Furuhara et al. [7], Ti–Mo-based systems exhibited a miscibility gap in the beta phase. However, on water quenching, Ti–Mo alloys also showed athermal omega precipitates. Thus Al, which is known to destabilize the beta to omega phase transformation [6], was added to the binary Ti–Mo alloy. An annealing temperature of 400 °C was chosen because at this temperature the kinetics of alpha precipitation is not too fast and the elemental partitioning of Mo and Al is not extremely diffusion limited. As per Ref. [6], for Ti–10 at.% Mo the beta phase miscibility gap is above 400 °C. Thus, for the current alloy (Ti–10Mo–10Al), the existence of phase separation in the beta matrix and the absence of any omega phase precipitation were expected as the starting conditions. On continued annealing at 400 °C, the influence of prior beta phase separation on the nucleation of alpha phase and concurrent solute partitioning before and after the alpha nucleation event have been investigated in this work.

Atom probe tomography (APT) has been shown to be extremely useful for analyzing the compositional partitioning associated with early stages of phase transformation in titanium alloys [8–10]. During independent APT analysis of the annealed Ti–Mo–Al ternary alloy,

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simultaneous partitioning of Ti, Mo and Al was observed. However, without any prior crystallographic information, associating these variations with the beta matrix and alpha precipitates, especially during the early stages of phase evolution, is difficult. In the current work, this inability to identify the precipitate–matrix interface by APT reconstruction alone inspired the transmission electron microscopy dark-field (TEM DF) imaging of an atom probe tip that was subsequently analyzed via APT. In recent years, a number of research groups have worked on the methodology, hardware and application of direct coupling of TEM and APT using the same holder [11–15]. In this study, information about the geometry of the sample and precipitate distribution obtained by TEM DF imaging of the APT needle sample is used as input data to optimize the subsequent APT reconstruction.

The Ti–10Mo–10Al alloy was fabricated using the Laser Engineered Net Shaping (LENS)™ process. The procedure of LENS™ deposition is described in detail elsewhere [16]. The "as-deposited" sample was homogenized and beta solution treated at 1000 °C for 30 min in an atmosphere-controlled furnace and subsequently water quenched. Sections of this water-quenched sample were annealed at 400 °C for 72 h and some sections were additionally annealed for 1 h at 600 °C. Site-specific TEM and APT samples were prepared from the annealed alloys using a focused ion beam (FIB)-based lift-out process using an FEI Nova Nanolab 200™ system [17]. For direct coupling of TEM and APT, FIB samples were attached on electropolished half-cut Cu TEM grids. These grids were mounted on a Hummingbird Scientific™ tomography holder for TEM DF imaging using a 200 kV FEI Tecnai F20™ microscope [11,12,15]. Three-dimensional atom probe analyses of the exact same samples were performed by loading the Cu grid, containing the atom probe samples, into a CAMECA LEAP 3000X HR™ atom probe and subsequently evaporating them. The samples were run in laser evaporation mode at 60 K with an evaporation rate of 0.5%. The APT data were reconstructed and analyzed using the commercial IVAS 3.6.0™ software.

Figure 1(a) shows a high-resolution TEM image of the Ti–10Mo–10Al alloy that was annealed at 400 °C for 6 h, viewed along the [0 0 1] beta zone axis. The Fourier-filtered image is shown in Figure 1(b), corresponding to the exact same region shown in Figure 1(a). Both these atomic-resolution images exhibit a high degree of strain contrast arising from the differences in the body-centered cubic lattice parameters in different regions of the sample. While all regions appear to be cubic, there are clearly at least two different lattice parameters, as evidenced by the fast Fourier transform (FFT) of Figure 1(a), shown as an inset in the same figure. Each of the primary beta reflections at (1 1 0) and (2 0 0) beta positions in the FFT pattern shown in Figure 1(a) has corresponding faint satellite reflections, attributable to the two different lattice parameters within the beta phase arising from phase separation. Additionally, further synchrotron as well as detailed TEM studies are currently underway to confirm beta phase separation in this alloy. A TEM bright-field (BF) image of the Ti–10Mo–10Al sample annealed at 400 °C for 72 h shows uniformly distributed clusters of multiple alpha phase variants within the beta matrix (Fig. 1(c)). The corresponding DF image, shown in Figure 1(d), was obtained using the alpha reflections, visible at the ½(1 1 2) beta positions, in the [1 1 0] beta zone axis diffraction pattern shown as an inset in Figure 1(c). The same diffraction pattern also shows double diffraction spots arising from the alpha reflections, and these have been circled. As evident from the TEM DF image (Fig. 1(d)), the size of an individual alpha lath within a cluster is roughly $\sim$100 nm in length and $\sim$10 nm in width. The morphology and distribution of this alpha phase in the Ti–10Al–10Mo alloy are very similar to the star-shaped cluster of plate-like precipitates that has been previously attributed to alpha phase nucleated from phase-separated beta [6].

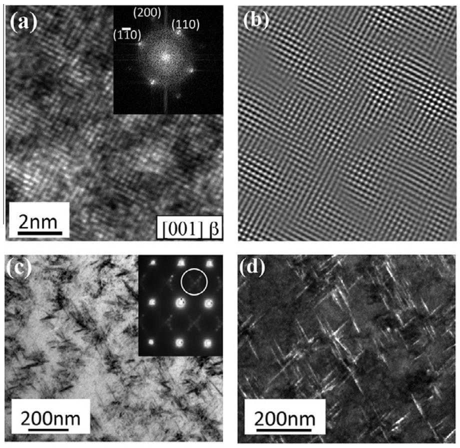

Figure 1. (a) High-resolution (HR) TEM image of Ti–10Mo–10Al alloy annealed at 400 °C for 6 h. The inset shows the FFT of the region. (b) Fourier-filtered HRTEM image corresponding to (a). (c) TEM BF image of Ti–10Mo–10Al alloy annealed at 400 °C for 72 h. The inset shows the [1 1 0] beta selected area diffraction pattern, with the specific alpha reflection chosen to form the DF image marked by a circle. (d) DF image of the same alloy showing alpha precipitate clusters with multiple variants.

Figure 2(a) shows the DF image of the atom probe sample before APT analysis. The sample tip diameter measured from the image, excluding the amorphous region along the edge, was about 16 nm and the half shank angle was approximately 13°. The angle between the two different variants of alpha laths located within the top 200 nm of the APT sample was approximately 106°. After the TEM imaging, APT analysis of the same sample was performed using laser evaporation with a 0.3 nJ laser pulse energy and a 60 K sample temperature. The parameters used for the three-dimensional reconstruction of the atom probe tip, such as the tip diameter and half shank angle, were calibrated based on the TEM DF images. Using an 88 at.% Ti isoconcentration surface, similar alpha variants were observed within the APT reconstruction shown in Fig. 2(b), consisting of a total of 2.1 million ions. The corresponding volume is shown by white dotted lines in the TEM DF image (Fig. 2(a)). Figure 2(c) shows the corresponding compositional variations in terms of proximity histogram profiles that were generated using the 88 at.% Ti isoconcentration surface. As expected, the plot clearly