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Atom-probe tomographic study of γ/γ' interfaces and compositions in an aged Co–Al–W superalloy

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Atom-probe tomography (APT) is utilized to investigate, in a Co–9.7Al–10.8W at.% alloy aged at 900 °C for ~1000 h, the phase compositions and partitioning behavior of the two-phase γ(face-centered cubic)/γ'($L1_2$) microstructure. The APT composition of the γ-matrix (Co–8.97Al–5.69W at.%) agrees well with a previously reported measurement made by energy-dispersive X-ray spectroscopy; however, the composition of the γ'($L1_2$) precipitates (Co–10.03Al–12.48W at.%) is slightly richer in W and Al, and leaner in Co. Partitioning coefficients and Al interfacial excesses are also calculated.

Keywords: Cobalt alloys; Superalloy; Atom-probe tomography; Intermetallic compounds; Interfaces

Nickel-based superalloys owe their excellent strength at ambient and elevated temperatures to their two-phase γ (face-centered cubic, fcc)/γ' ($L1_2$) microstructure consisting of coherent γ'-Ni_3Al-based precipitates in a disordered fcc γ-Ni–Al based matrix [1–4]. Until recently, it was believed that analogous Co-based γ/γ' structures did not exist, thus relegating Co-based alloys to applications at moderate temperatures and stresses. In 2006, Sato et al. discovered in the Co–Al–W ternary system a γ(fcc)/γ'($L1_2$) microstructure analogous to that of Ni-based superalloys [5]. The Co–Al–W phase diagram presented by Sato et al. [5] shows that, at 900 °C, the γ/γ' two-phase region is significantly narrower than in the Ni–Cr–Al phase diagram, stressing the importance of knowing the exact compositions of both phases, lest the Co–Al–W alloy deviates to one of the surrounding three-phase field regions with embrittling phases. High-temperature flow-stress [6,7] and creep measurements [8–10] of the γ/γ' Co–Al–W superalloys with quaternary and higher alloying additions have shown promise for continued development for high-temperature applications. Due to the rather limited literature available on the Co–Al–W system, further validation is necessary to better characterize this phase diagram at equilibrium and the microstructural evolution including the evolution of the γ- and γ'-phase compositions during nucleation, growth and coarsening. Understanding the evolution of these phases is essential as they exhibit strong deviations from their equilibrium values in γ/γ' Ni–Cr–Al superalloys [11,12]. To date, very few compositional measurements have been reported in the literature. The original phase diagram proposed by Sato et al. remains the standard, and few additional reports exist on characterizing the Co–Al–W phase diagram. Some have measured the γ-compositions in multiphase systems but have not reported the γ'-compositions due to questions concerning phase stability [13,14], while others have attempted to cast single-phase γ'-ingots to study the mechanical properties of the $L1_2$ phase [15–18]. Of all the single-phase γ'-alloys, Co–10Al–11W at.% was the only composition investigated that did not contain secondary phases. Recently, Meher et al. [19] used atom-probe tomography (APT) to measure the composition of a ternary Co alloy at 765 °C; additional investigation is, however, necessary to further develop the phase diagram of this promising new class of Co-based alloys.

Herein, the nanostructure of a homogenized and aged Co–Al–W ternary alloy is examined utilizing an ultraviolet laser-assisted local-electrode atom-probe (LEAP) tomograph, which provides precise compositions of the γ- and γ'-phases. Given the narrow range of composition of the γ/γ' two-phase field in this ternary alloy,

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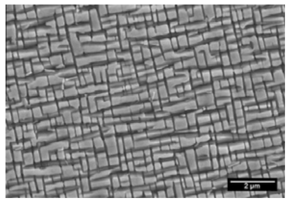

Figure 1. Secondary electron SEM micrograph of etched Co–9.7Al–10.8W aged at 900 °C for 1006 h. The light contrast reveals cuboidal γ'-precipitates, while dark contrast indicates the γ-matrix channels that have been selectively etched.

these precise compositions are essential for alloy manufacturing. Additionally, the subnanometer-level spatial resolution of the LEAP tomograph provides detailed information on partitioning between the two phases and segregation behavior at the matrix/precipitate interface in a Co–Al–W alloy, which has previously been reported for Ni–Cr–Al alloys [11,20].

The alloy was prepared by arc-melting 99.95% Co, 99.999% Al and 99.97% W under argon gas. Cast ingots were homogenized at 1300 °C for 2 h, aged at 900 °C for 1006 h (~42 days) and subsequently quenched in water. The homogenized alloy composition was Co–9.3Al–11.0W, as measured on polished samples by energy-dispersive X-ray spectroscopy (EDS) using a Hitachi[1] field-emission scanning electron microscope (SEM), S4700. Standards for each element were used in the EDS analysis. SEM microstructure imaging was performed on aged samples etched with a solution of 100 ml deionized H_2O, 10 ml of 65% HNO_3, 50 ml of 32% HCl and 10 g of $FeCl_3$. APT specimens were fabricated using an FEI Helios Nanolab microscope, equipped with an electron gun and a Ga focused ion beam (FIB). Three microtips were sharpened with Ga^+ ions to ~50 nm radius, with a final FIB energy of 5 keV at a current of 16 pA. APT measurements were performed with a Cameca 4000X-Si LEAP tomograph with a picosecond ultraviolet (wavelength = 355 nm) laser energy of 30 pJ per pulse, a pulse repetition rate of 200 kHz, a microtip temperature of 35 K, and evaporation rates (ion per pulse) of 3% for microtip 1 and 5% for microtips 2 and 3. These conditions were chosen based on a calibration study of the homogenized Co–9.3Al–11.0W alloy, in which the composition was measured as a function of laser pulse energy, microtip temperature, pulse repetition rate and evaporation rate. During this study it was found that the composition of the homogenized sample as measured by APT was Co–9.65Al–10.77W. All results were analyzed using Cameca's IVAS 3.6.2 APT software.

Figure 1 shows an SEM micrograph of a representative etched cross-section of the alloy. The structure consists of a high volume fraction of γ' ($80 \pm 4\%$) as determined by the line intercept method measured from backscattered SEM micrographs of unetched samples oriented near the

[1] Certain commercial equipment, instruments or materials are identified in this article to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

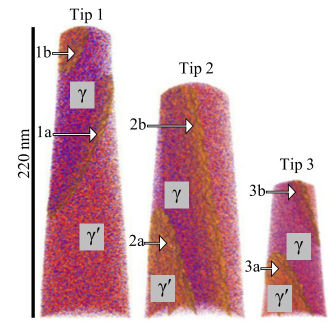

Figure 2. APT three-dimensional reconstructions of microtips 1-3, where the γ/γ' interfaces are indicated by 8.6 at.% W isoconcentration surfaces. Arrows indicate the six γ/γ' interfaces present in the microtips. The Co, Al and W atoms are represented in blue, red and orange, respectively. Each spot indicates a single atom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

001-orientation, which is in agreement with the $83 \pm 5\%$ calculated from pixel counting image analysis of the same micrographs. Figure 2(a–c) displays APT reconstructions for microtips 1, 2 and 3, which contain 30, 38 and 8 million atoms, respectively. Ga contamination from ion milling was <0.009 at.%. As anticipated (Fig. 1), γ'-precipitates are too large to be fully encompassed in an APT microtip, so the reconstructions exhibit only partial γ'-precipitates. The γ/γ' interfaces in Figure 2(a–c) are represented by orange 8.6 at.% W isoconcentration surfaces. All microtips contain a γ-channel between two γ'-precipitates imaged partially due to their large size. As anticipated from the SEM image of closely packed cuboidal precipitates (Fig. 1), all γ/γ' interfaces are planar with the exception of interface 3b in microtip 3, which contains a slight degree of curvature. Subsequent transmission electron microscopy (TEM) on the aged sample revealed a very small amount of μ-phase, which was not observable by SEM analysis. The small volume fraction is unlikely to affect the compositional results of the γ- and γ'-phases.

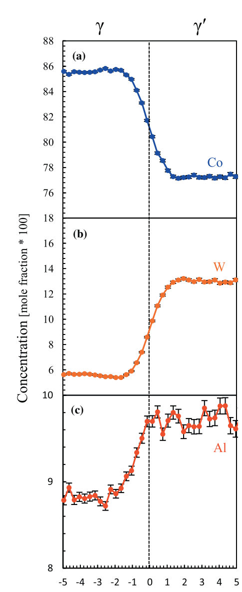

Figure 3. Proximity histograms of the five interfaces displayed in Figure 2, for (top) Co, (middle) W and (bottom) Al.