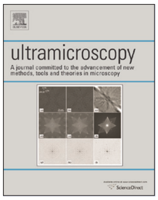
Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic



Determination of solute site occupancies within γ′ precipitates in nickel-base superalloys via orientation-specific atom probe tomography

S. Meher [a,1], T. Rojhirunsakool [a], P. Nandwana [a,2], J. Tiley [b], R. Banerjee [a,*]

[a] *Center for Advanced Research and Technology, Department of Materials Science and Engineering, University of North Texas, Denton, TX, USA*
[b] *Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, OH, USA*

ARTICLE INFO

Article history:
Received 4 September 2014
Received in revised form
8 April 2015
Accepted 23 April 2015

Keywords:
Nickel-base superalloys
APT
EBSD
Site occupancy
SDM

ABSTRACT

The analytical limitations in atom probe tomography such as resolving a desired set of atomic planes, for solving complex materials science problems, have been overcome by employing a well-developed unique and reproducible crystallographic technique, involving synergetic coupling of orientation microscopy with atom probe tomography. The crystallographic information in atom probe reconstructions has been utilized to determine the solute site occupancies in Ni–Al–Cr based superalloys accurately. The structural information in atom probe reveals that both Al and Cr occupy the same sub-lattice within the $L1_2$-ordered γ′ precipitates to form $Ni_3(Al,Cr)$ precipitates in a Ni–14Al–7Cr (at%) alloy. Interestingly, the addition of Co, which is a solid solution strengthener, to a Ni–14Al–7Cr alloy results in the partial reversal of Al site occupancy within γ′ precipitates to form $(Ni,Al)_3(Al,Cr,Co)$ precipitates. This unique evidence of reversal of Al site occupancy, resulting from the introduction of other solutes within the ordered structures, gives insights into the relative energetics of different sub-lattice sites when occupied by different solutes.

1. Introduction

Nickel-base superalloys have been extensively used as materials for high temperature applications because of their ability to form coherent ordered γ′ precipitates within the face centered cubic matrix (γ), which enables the retention of high strength close to their melting temperature [1]. The key factors, based on thermodynamic and kinetic principles, for alloy development are controlled partitioning of solute elements between the matrix (γ) and the precipitates (γ′), and the solute site occupancy within the γ′ phase. As the γ′ precipitates are coherent with the matrix, the relative compositions of these phases determine the lattice coherency and subsequent high temperature microstructural changes and mechanical properties [2]. On the other hand, the site occupancy of various solutes within the γ′ precipitates can influence the ductility of the precipitates and the ordering energy, which can affect the precipitation strengthening in Ni-base superalloys [3]. Co is a main alloying element, present in many commercially available Ni-superalloys [1]. Co has been reported to increase the high temperature mechanical strength by reducing the stacking fault energy of γ matrix [4]. It is also reported that high level of Co addition can alter the partitioning behavior of other solute atoms, preventing the formation of detrimental phases [5].

There have been many attempts to study the sub-lattice site occupancies of various solutes in ordered compounds using atom probe tomography (APT) [3,6,7]. Over the last few decades, APT has been the technique of choice for compositional analysis in many metallic materials due to its inherent capability for the element-specific quantitative probing at sub-nanometer scale. The occasional high resolution in atom probe can resolve the individual lattice planes and various structural analyses in metallic alloys including solute site occupancy in γ′ precipitates in Ni-base superalloys have been reported earlier [3,6–13].

The currently reported articles on advancement in atom probe tomography for exploration of the crystallographic information, retained in the reconstructions, are based on implementation of algorithms like Fourier transforms and Hough transforms to the atom probe dataset [14–16]. These algorithms have successfully indexed the crystallographic poles within the ion desorption image, formed by accumulation of ions onto the detector, in pure

---

[*] Corresponding author. Fax: +1 940 565 4824.
E-mail address: rajarshi.banerjee@unt.edu (R. Banerjee).
[1] Presently at Department of Materials Science and Engineering, Idaho National Laboratory, Idaho Falls, Idaho, USA.
[2] Presently at Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

http://dx.doi.org/10.1016/j.ultramic.2015.04.015
0304-3991/© 2015 Elsevier B.V. All rights reserved.

Please cite this article as: S. Meher, et al., Determination of solute site occupancies within γ′ precipitates in nickel-base superalloys via orientation-specific atom probe tomography, Ultramicroscopy (2015), http://dx.doi.org/10.1016/j.ultramic.2015.04.015

metals or dilute alloys and have been employed for three-dimensional (3D) orientation mapping of grain boundaries in nanocrystalline materials and solute site occupancies [6,14]. However, the large difference in the evaporation field associated with multiple elements in superalloys yield low contrast in the desorption image [17]. Thus, the utilization of these algorithms for a comprehensive crystallographic study in multi-component complex alloys is still challenging.

In some recent works, orientation microscopy has been coupled with APT, for various microstructural characterizations [18–21], but the use of this technique for precise site occupancy determination in Ni-base superalloys is still unknown. The structural and compositional information, obtained utilizing this method, has determined the solute site occupancies in γ′ precipitates in some Co-based superalloys [22].

In the present paper, a unique and reliable experimental approach reported by Meher et al. [23] has been employed, which can extract crystallographic information in the APT datasets of highly alloyed and polycrystalline superalloys by coupling orientation microscopy with APT. This characterization method involving the electron backscattered diffraction (EBSD) mediated precise site-specific sample preparation is an alternate method enabling the crystallographic study of complex multi-phase materials, which is demonstrated in the present study of Ni–Al–Cr and Ni–Al–Cr–Co alloys.

2. Experimental

The as-cast nominal Ni–14Al–7Cr (at%) and Ni–14Al–7Cr–16Co (at%) alloys were encapsulated in quartz tubes backfilled with argon and were heated in a furnace at 1200 °C in the single γ phase field for 1 h, followed by water quenching. The homogenized samples were encapsulated again, annealed for 256 h at 800 °C to achieve near equilibrium phase compositions, and finally, water quenched. Microstructural imaging and bulk composition determination were carried out in a FEI Nova 230NanoSEM field emission gun scanning electron microscope equipped with backscatter detector. Electron backscatter diffraction (EBSD) studies were done on these samples prepared by standard metallographic methods in a dual-beam focused ion beam (dual-beam FIB) instrument, the FEI FESEM NOVA 200, retrofitted with EDAX Digi-View IV EBSD camera. TSL OIM Data Collection and TSL OIM Data Analysis 5.3 software were used for data acquisition and analyses respectively. Since the γ′ precipitates typically exhibit a cube-on-cube orientation relationships with the γ matrix, a γ grain close to ⟨001⟩ crystallographic orientation was identified and the atom probe samples were subsequently extracted from that region using dual-beam FIB. APT was carried out using a local electrode atom probe (LEAP^{TM} 3000X) system in the voltage evaporation mode at a temperature of 40 K, with an detection rate about 0.5 ion/pulse and a pulse frequency of 200 kHz. Data analysis was performed using the IVAS 3.6.6 software.

3. Results and discussion

Fig. 1(a) shows a backscattered scanning electron microscopy (SEM) image of a long-term annealed sample of Ni–14Al–7Cr (at%), where the near spherical γ′ precipitates, with a high number density, are uniformly dispersed in a γ matrix. The size scale of γ′ precipitates ranges from 150 to 200 nm. Fig. 1(b) shows the pole figure of the particular grain used for the site-specific FIB lift-out, that confirms an offset of 2° from the ⟨001⟩ pole. Fig. 1(c) shows the secondary SEM image of the atom probe tip, prior to the final ion-polishing step in the FIB, which shows that the alignment of the γ/γ′ interfaces is nearly perpendicular to the axis of the tip, as expected from the pole figure. Fig. 1(d) is the 2D desorption image from the APT data, which exhibits a central ⟨001⟩ pole with four other poles clearly exhibiting a four-fold symmetry. The appearance of clear crystallographic poles in the desorption image of this complex multi-component material, despite large differences in the evaporation fields associated with these solute elements, is a clear indication of a well-controlled evaporation sequence in this experiment. Moreover, the coincidence of the position of the central ⟨001⟩ pole relative to the center of the desorption image indicates the minimal mis-orientation of the tip axis from ⟨001⟩ direction. Fig. 1(e) shows the APT reconstruction, which clearly exhibits a flat horizontal γ/γ′ interface (14 at% Al iso-concentration surface), confirming the accuracy of the proposed technique.

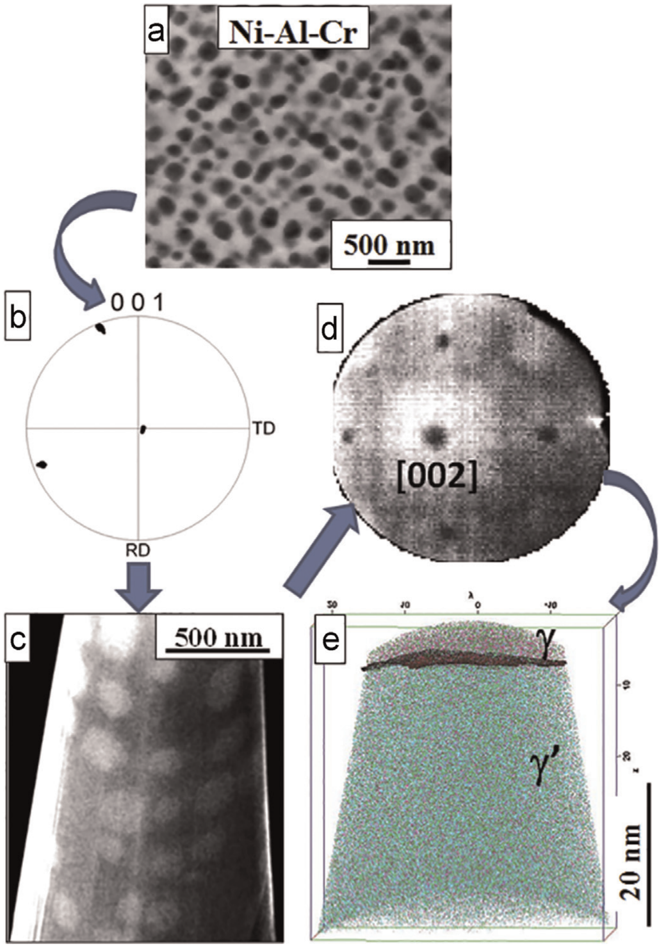


Fig. 1. (a) Backscattered SEM micrograph of Ni–14Al–7Cr (at%) showing dispersion of spatially correlated γ′ precipitates in a γ matrix, (b) EBSD pole figure showing the dual-beam FIB lift-out to be closer to ⟨001⟩ axis with an offset of 2°, (c) the pre-final tip prepared using dual-beam FIB shows alignment of precipitates along ⟨001⟩ direction with minimal offset, (d) 2D desorption image show poles and zone lines with central ⟨001⟩ pole, having an four-fold symmetry, and (e) APT reconstruction show a near horizontal γ–γ′ interface.

Fig. 2(a) shows a proximity histogram (proxigram) [24], created using the 14 at% Al isosurface, clearly exhibiting the compositional profiles for Al and Cr across the γ/γ′ interface. The summation of Al and Cr content within the γ′ precipitates equals 25 at%. With the assumption of an ideal stoichiometry for this L1_2 phase, the ratio of Ni-sublattice sites (1/2,1/2,0 type) to Al-sublattice (0,0,0 type) sites should be 3:1. Since the summation of Al and Cr equals 25 at%, the partitioning of solutes between the Ni and Al sublattice sites appears to be such that both Al and Cr exclusively occupy the Al-sublattice sites, while Ni atoms exclusively occupy the Ni-

Please cite this article as: S. Meher, et al., Determination of solute site occupancies within γ′ precipitates in nickel-base superalloys via orientation-specific atom probe tomography, Ultramicroscopy (2015), http://dx.doi.org/10.1016/j.ultramic.2015.04.015