Dependence of interfacial excess on the threshold value of the isoconcentration surface

Kevin E. Yoon,1 Ronald D. Noebe,2 Olof C. Hellman3 and David N. Seidman1*

1 Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA
2 NASA Glenn Research Center, Cleveland, OH 44135, USA
3 Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195, USA

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The proximity histogram (or proxigram for short) is used for analyzing data collected by a three-dimensional atom probe microscope. The interfacial excess of Re (2.41 ± 0.68 atoms nm⁻³) is calculated by employing a proxigram in a completely geometrically independent way for γ/γ interfaces in René N6, a third-generation single-crystal Ni-based superalloy. A possible dependence of interfacial excess on the variation of the threshold value of an isoconcentration surface is investigated using the data collected for René N6 alloy. It is demonstrated that the dependence of the interfacial excess value on the threshold value of the isoconcentration surface is weak. Copyright © 2004 John Wiley & Sons, Ltd.

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INTRODUCTION

Three-dimensional atom probe microscopy¹–³ has been developed to produce three-dimensional atom-by-atom reconstructions of field ion microscopy specimens. Three-dimensional atom probe microscopy combines a two-dimensional position-sensitive detector, which gives lateral information (x- and y-positions) and a time-of-flight mass spectrometer, which yields the chemical identity of each field-evaporated ion. The process of field evaporation allows one to explore the interior of a specimen on an atom-by-atom basis. The lateral spatial resolution within a crystallographic plane is ≈0.3–0.5 nm, which is limited by physical aberrations associated with the field evaporation process. In the z-direction, however, subnanoscale resolution is achieved due to the ability to dissect an atomic plane on an atom-by-atom basis, which implies an atomic plane-by-plane analysis capability with a depth resolution equal to the interplanar spacing. By employing a three-dimensional atom probe microscope, it is therefore possible to construct elemental distributions in real space and perform chemical analyses of internal interfaces (grain boundaries or heterophase interfaces) and nanoparticles with subnanometer scale resolution. Three-dimensional atom probe microscopy is particularly appropriate for nanoscale chemical studies of complex commercial alloys containing a large number of alloying elements.

The proximity histogram (or proxigram for short)⁴ method is a data analysis technique that we have developed to generate concentration profiles associated with interfaces in a geometrically independent way. This analysis technique integrates the chemical and three-dimensional positional information and then generates an atomic fraction versus distance to interface histogram for all the interfaces in a specimen, in parallel, delineated by the isoconcentration surface. In addition, it does not require choosing any arbitrary axis or geometric subvolume. Therefore, the proxigram can be used to generate concentration profiles for data sets containing many interfaces and thereby readily detect interfacial excesses for all the internal interfaces in an analyzed volume in parallel.

In the present research, a third-generation Ni-based superalloy, René N6, which has been developed by General Electric Corporation⁵ for turbine engine blade materials, was investigated by three-dimensional atom probe microscopy at Northwestern University. Segregation of Re at the γ/γ interface was observed and the interfacial excess was determined using the proxigram method. The sensitivity of the interfacial excess value on the threshold value of the isoconcentration surface was examined by calculating the interfacial excess values for a range of threshold values, thereby demonstrating that the value of the interfacial excess is only weakly dependent on the threshold value.

EXPERIMENTAL

An ingot of a single crystal of René N6 was supplied by General Electric Corporation in the as-heat-treated state. The material was given a final solution heat-treatment at 1330°C for 6 h and then received a proprietary three-stage aging heat treatment. Atom probe specimens were cut from this alloy into 0.2 × 0.2 × 2 mm³ blanks using electrical discharge machining. A standard electrochemical polishing technique was employed, using 2 vol.% perchloric
Plate 1. Three-dimensional atom-by-atom reconstruction of the second data set containing 1 million atoms with an isoconcentration surface of Cr at a threshold value of 7 at.%. The positions of Al atoms are displayed in red, Ta in light pink, Cr in blue, W in light blue, Re in yellow and Mo in dark green. The Ni, Co and Hf atoms are not exhibited in this figure for the sake of clarity.
acid in butoxyethanol electrolyte, to obtain sharp needle-like tips with an apex radius of \( \leq 0.5 \) nm. Field ion microscopy images were obtained at 60 K using Ne as the imaging gas (10\(^{-6}\) Torr). Atom probe analyses were conducted under ultrahigh vacuum (UHV) conditions (<10\(^{-9}\) Torr gauge pressure) at 40 K with a pulse fraction, \( f \), of 0.19 (\( f \) is the ratio of the pulse voltage to the steady-state d.c. imaging voltage) and a pulse frequency of 1.5 kHz. An energy-compensated atom probe\(^3\), with an optical detection system\(^4\) was used for the analyses. The data analyses were performed using ADAM 1.5\(^7\) software. ADAM 1.5 is a custom Macintosh application currently employing OS9, developed at Northwestern University specifically to analyze data generated by a three-dimensional atom probe microscope.

**RESULTS AND DISCUSSIONS**

A total of 1.4 million ions were collected from one sample. The collected data were divided into two data sets (400,000 and 1 million ions) for the convenience of computer analyses and were analyzed utilizing ADAM 1.5. The first data set contains a \( \gamma/\gamma' \) interface that is perpendicular to the analysis direction, whereas the second data set contains a \( \gamma/\gamma' \) interface that is parallel to the analysis direction. A three-dimensional reconstruction of the collected microscope data is shown in Plate 1 (for the second data set). The positions of Al atoms are indicated in red, Ta atoms in light pink, Cr atoms in blue, W atoms in light blue, Re atoms in yellow and Mo atoms in dark green. The Ni, Co and Hf atoms are not displayed for the sake of clarity. The location of the \( \gamma/\gamma' \) interfaces in the specimen is identified by a Cr isoconcentration surface with a threshold value of 7 at.\%; it is emphasized that the proxigram methodology simultaneously measures all the interfaces in a given data set, which is important for obtaining statistically significant data rapidly. Segregation of Re cannot be seen on this plate due to the large number of alloying elements in René N6. The qualitative partitioning behavior of alloying elements can, however, be observed from the color-coding of atoms and the results agree qualitatively with a report on the superalloy CMSX-4.\(^8\) Bulk elemental compositions of the sample were determined by counting the number of atoms detected. The precipitates and matrix phase compositions are determined from the plateau regions of each proxigram. The error in concentration is represented by the standard deviation \( \sigma \)

\[
\sigma = \sqrt{\frac{C_i(1-C_i)}{N}}
\]

which was determined by employing standard counting statistics. The quantity \( C_i \) is the measured atomic concentration of element \( i \) and \( N \) is the total number of atoms detected.

First, the isoconcentration surface of Cr was generated in a three-dimensional reconstruction by using a threshold value of 7 at.\% Cr (Plate 1). This Cr isoconcentration surface serves as a reference surface for constructing the proxigram. The threshold value was chosen from the inflection point in the Cr profile (see Fig. 2, the first data set) and this determines the reference point (i.e. \( x = 0 \)) of the proxigrams (see Figs 1–3). This means that the concentration of Cr at \( x = 0 \) is 7 at.\% Cr in Fig. 2. The reason for choosing the threshold value by employing the inflection point is explained in detail below. By using this 7 at.\% Cr isoconcentration surface the concentration of Re can be calculated at specific distances from all the \( \gamma/\gamma' \) interfaces in the data set and converted to a proxigram by plotting the atomic fraction of Re versus the distance from the interface. The interfacial excess value was calculated from this proxigram by using a planimeter to measure the area under the concentration profile at the interface, where the excess Re is located (Fig. 1). It is strongly emphasized that Fig. 1 contains three-dimensional information because the proxigram method integrates over two of the six faces of the cuboidal \( \gamma' \) precipitates; the precipitates have a mean edge length of 500 nm, which is a significant fraction of the tip diameter and therefore it is difficult to sample all six faces of the cuboidal precipitates simultaneously. However, in a model Ni–Al–Cr base superalloy with considerably smaller precipitate diameters we are able to analyze all six faces simultaneously.\(^9\)

To investigate the sensitivity of the Re excess value on the threshold value, five different proxigrams were generated by employing five different threshold values (4, 6, 6.5, 7 and 8.1 at.\% Cr) for the first data set. For the second data set, four threshold values (4.9, 5.5, 7 and 10 at.\% Cr) were used. All the threshold values were chosen arbitrarily from the concentration values that are located in the steepest portion of the concentration gradient of the Cr profile (Fig. 2). This was done in order to acquire a physically meaningful isoconcentration surface, which is located within the width of the real \( \gamma/\gamma' \) interfaces. Different Cr threshold values were utilized for each data set to guarantee this point. The proxigram for Cr for the first data set is exhibited in Fig. 2 and the proxigrams for Re for both data sets are displayed in Fig. 3. All the proxigrams of Re display significant excesses of Re at the \( \gamma/\gamma' \) interfaces. The calculated interfacial excess

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**Figure 1.** A proxigram displaying the Re atomic fraction as a function of distance with respect to the \( \gamma/\gamma' \) interface; positive values are into the matrix (\( \gamma' \)) and negative values are into the precipitate (\( \gamma' \)). The interface is defined by an isoconcentration surface at 7 at.\% Cr (Plate 1). The interfacial excess of Re is indicated by the gray region.
The interfacial excess $\Gamma_i^{\text{excess}}$ is expressed by the following equation:

$$\Gamma_i^{\text{excess}} = N_i^{\text{excess}} / A$$  \(1\)

where $N_i^{\text{excess}}$ is the excess number of $i$ atoms at the interface and $A$ is the area of the interface. The excess value is therefore an excess quantity per unit interfacial area and depends on the arbitrary choice of the location of the so-called Gibbs dividing surface. In the proxigram method, the isoconcentration surface acts as the dividing surface. Theoretically, the excess value should differ as the threshold value is varied, because the specific location of the dividing surface moves as the threshold value is changed. The chosen threshold values are, however, located at the steepest part of the concentration gradient of the Cr profile in the proxigram (Fig. 2). Consequently, the amount of positional shift is minimized. In addition, the proxigram calculates the concentration of Re in three-dimensional real space and measures the shortest distance from a specific atomic position to the isoconcentration surface. This calculation technique for the proxigram makes the detailed topological complexity of the surface irrelevant for the calculation, i.e. it does not require the interface to be flat. As a result, a change in threshold value for the isoconcentration surface only changes the position of the reference point (i.e. $x = 0$ in the proxigram) and not the shape of the concentration profile in the proxigram, as seen in Fig. 3. The shift in the position of the reference point does not significantly affect the shape of the profile, so the area under the profile at the peak remains essentially constant. As a result, the dependence of the interfacial excess value on the threshold value of the isoconcentration surface is weak.
CONCLUSIONS
A complex commercial René N6 Ni-based superalloy, which contains nine alloying elements, was investigated by three-dimensional atom probe microscopy and segregation of Re was observed at the γ'/γ' interfaces. The interfacial excess of Re, $\Gamma_{\text{Re}}$, is calculated from the proxigram method and its average value is $2.41 \pm 0.68$ atoms $\text{nm}^{-2}$ ($2.41 \pm 0.68 \times 10^{14}$ atoms $\text{cm}^{-2}$), using the average atomic density (83 atoms $\text{nm}^{-3}$) of the γ matrix. The values of $\Gamma_{\text{Re}}$ are independent of whether the γ'/γ' interface is parallel or perpendicular to the direction of analysis.

The dependence of the excess value on the threshold value of the isoconcentration surface was examined by varying its value for nine different values (4, 6, 6.5, 7 and 8.1 at.% Cr for the first data set and 4.9, 5.5, 7 and 10 at.% Cr for the second data set) and then calculating the excess value for Re at γ'/γ' interfaces in René N6. Our results demonstrate that the sensitivity of the value of the excess on the threshold value associated with an isoconcentration surface is small for René N6.

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