Systematic procedures for atom-probe field-ion microscopy studies of grain boundary segregation

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(Received 6 March 1992; accepted for publication 31 May 1992)

A procedure is presented for systematically and reproducibly preparing alloy specimens for the study of grain boundary (GB) segregation employing both transmission electron (TEM) and atom-probe field-ion microscopies (APFIM) to examine the same GB; the procedure is illustrated for an Fe(Si) alloy. A commercially available oxygen plasma source is incorporated in the sample preparation procedure to remove all traces of hydrocarbon build-up introduced during TEM GB analysis, thus allowing controlled backpolishing after a TEM analysis. Specifications for the optimum tip geometry, i.e., how a GB is positioned in a tip via backpolishing to maximize the probability of its observation and subsequent compositional analysis via APFIM, are empirically determined: 30–200 nm for the GB-to-tip separation, and 40–80 nm for the GB diam for shank angles less than 20°. It is demonstrated that accurate quantitative APFIM analyses of an Fe-3 at. % Si alloy are possible for pulse fractions >15% and specimen temperatures <55 K. Results are presented for a Σ₇=3 GB that was first analyzed via TEM to determine its five macroscopic degrees of freedom, and then analyzed via APFIM to measure an average GB segregation enhancement factor for Si of 3.51 ± 0.34 at 823 K.

I. INTRODUCTION

The phenomenon of equilibrium solute-atom segregation at grain boundaries (GBs) is important because of the role that the GB composition plays in determining the mechanical and physical properties of materials. For example, in steels, the impurities Si, Sn, Sb, and P induce temper embrittlement by segregating to GBs during heat treatments between 673 and 873 K.¹ Additions of B; N, and S to an Fe-6 at. % Si transformer steel produce a high permeability steel by segregating to GBs during recrystallization of a GB's structure, a knowledge of the relationship between the properties of a material and GB composition.

II. SPECIMEN PREPARATION

There are four requirements that a specimen preparation procedure must satisfy: (1) the tip of a specimen must be electron transparent and clean at 200 kV (<0.7-nm diameter); (2) the tip must be sharp (≈50-nm diameter) and have a small shank angle (≈15° for the full cone angle) for APFIM; (3) after TEM analysis, the tip must be backpolished in a highly controlled manner (removal of <20-nm length of the tip per 1 ms of voltage pulse applied to an electrolytic cell) to bring a GB into the tip region for APFIM analysis; and (4) the final tip geometry, i.e., how
a GB is situated in the tip region must meet specifications
to maximize the probability of the observation and subse-
quent compositional analysis of the GB via APFIM. For
the ease of pure and low-alloy iron specimens, the tasks of
making a sharp and clean tip have been solved. Procedures exist for backpolishing, but they do not work for
specimens that have hydrocarbon contamination from
TEM analysis; this is an unavoidable problem because a
specimen is first analyzed via TEM to determine its five
macroscopic DOF and then backpolished to achieve a final
tip geometry. If a specimen is first backpolished to achieve
a final tip geometry, then the grain at the tip consists of a
volume too small to form a Kikuchi pattern and so accurate
GB analysis is not possible. The final tip geometry is
critical in the case of Fe(Si), as Si causes atomic disorder
in an FIM image making the traditional method of GB
identification difficult, i.e., observing atomic mismatch
across a GB plane, unless the GB plane passes through
low-index poles. In addition, the presence of Si at a GB
does not give rise to observable contrast effects in an FIM
image. GB identification, therefore, relies heavily on the
presence of a sufficient number of low-index poles in an
FIM image, so that the GB plane passes through at least
one of these poles. The tip geometry is also important be-
cause we have found that tips fracture when high voltages
are utilized.

A. Tip sharpening and controlled backpolishing

The electropolishing apparatus and special TEM
holder for preparing and analyzing specimens were de-
scribed earlier. Achieving a sharp tip on a Fe-3 at. % Si
specimen requires a two-step procedure: (1) An initial
taper on a 185-μm-diam wire is produced by electropolish-
ing at 18 Vdc in a 25% perchloric acid (70%)/75% acetic
acid solution—all solution percentages refer to volume
—using a beaker electrolytic cell. (2) A final polishing
to produce a sharp tip is performed in a zone electrolytic
cell at 22 Vdc with a 1% perchloric acid/99% 2-
butoxyethanol solution. During zone electropolishing, the
solution must be replenished frequently to prevent collec-
tion of contamination on a tip. For some specimens it is
necessary to add an additional step between the first and
second, that is, to employ 24 Vdc during zone electropol-
ishing until the tip is almost sharp enough for APFIM.
This intermediate step is necessary because of preferential
GB etching at 22 Vdc. The final electropolishing step is
performed at 22 Vdc, as 24-Vdc pits the surface. For this
step, the sample is quickly passed once through the cath-
ode loop of a zone electropolisher to provide a polishing
time sufficient to remove etch pits; this procedure removes
as little as 6 μm of length of a tip, and so is also used to
search further down the shank of a specimen for a GB.
Zone electropolishing is advantageous for GB studies by
providing control over the shank angle such that a rela-
tively large tip area can be made electron transparent. A

Controlled backpolishing of an FIM tip is accom-
plished using the beaker method with a 1% perchloric
acid/99% 2-butoxyethanol solution at 265–271 K. Fresh
electrolytic solutions and sources of perchloric acid and
2-butoxyethanol are used to prevent a tip from becoming
permanently contaminated during backpolishing; this con-
tamination makes further backpolishing impossible. The
electrolytic solution is cooled to prevent pitting and to al-
low the removal of small amounts of material per applied
voltage pulse. At temperatures <258 K, a passivating layer
forms on a tip and this layer inhibits further backpolishing.
The solution is cooled by a cold plate with magnetic stir-
rung capability (Thermoelectrics Unlimited Incorporated,
Wilmington, Delaware). The solution is constantly stirred
to replenish the electrolyte and to minimize temperature
gradients at the tip. Superinsulation is wrapped around a
beaker to maintain a temperature gradient between a point
a few mm below the top of the liquid surface and the bot-
tom of the beaker to within 0.1 K. A thermocouple fabri-
cated from 500-μm-diam wires is used to monitor the
temperature. The pulse height applied to the electrolytic
cell is 12 Vdc for pulse widths in the range 4–100 ms. For
pulse widths in the range 1–3 ms, pits begin to form on a
tip and so the voltage is reduced to 11 Vdc and the tem-
perature of the solution is decreased to 269.5 K. If the T is
decreased further to 268.5 K, then the voltage remains at
12 Vdc. The leading and trailing edges of an applied pulse
cannot have large negative-going excursions as iron is elec-
trodeposited back onto the tip, interfering with subsequent
backpolishing. A resistor and capacitor are placed in series,
to ground, between the power supply output and the elec-
trolytic cell cathode—see Fig. 1—to prevent violent pitting
that literally rips off a tip.

Figure 2 is an example of a tip that was sharpened and
then backpolished. Figure 2(a) is a specimen containing
two GBs before backpolishing was commenced. Figures
2(b)–2(e) show the use of backpolishing to bring one of
the two GBs—indicated by black arrows—to a tip. Under-
neath each TEM micrograph are indicated the total
eassembled electropolishing time and the rate of material re-
moved, in nm ms⁻¹, as measured along the length of the
tip. Another example is exhibited in Fig. 3. Below Figs.
3(a)–3(c) are both the total elapsed time of polishing in
ms and the rate of material removed in nm ms⁻¹ in a
direction along the length of the tip. The backpolishing
examples in Figs. 2 and 3 were performed at T=265 K and
V=11 Vdc. Figure 4 is an example of a tip that was back-
polished at T=270 K and V=12 Vdc. For this specimen

FIG. 1. Block diagram showing the RC circuit placed between the power
supply output and the electrolytic cell in order to obtain controlled back-
polishing.
the GB plane is perpendicular to the tip axis. This GB orientation is the ideal geometry for our GB segregation studies, because the GB composition is determined directly without data deconvolution for this geometry. Because these GBs are not at a large angle to the tip axis, the backpolishing conditions have to be well understood to prevent removing a GB during backpolishing. These three examples demonstrate that the backpolishing can be controlled so that the rate of material removed is less than 20 nm ms⁻¹.

FIG. 3. (a)–(c) represent an example of backpolishing of an Fe-3.0 at.% Si alloy specimen. Underneath each micrograph is the total elapsed backpolishing time. Below (b) and (c) are also the rate of removal of material (nm ms⁻¹) along the length of the tip. (d) is the specimen in (c) after field evaporation in our atom-probe field-ion microscope. This is an example of a grain boundary that was brought too close to a tip to observe it via field-ion microscopy. As discussed in Sec. II C, the tip in (a) is more suitable for APFIM. The distance from the tip apex to the top position of the GB (93 nm) and the diam of the GB at the top position (36 nm) and the bottom position (36 nm) of the GB are close to the optimal range for the observation and subsequent compositional analysis of a GB via APFIM.

B. Hydrocarbon contamination

Prior to backpolishing a specimen, the five macroscopic DOF of a GB in the specimen are determined using a Kikuchi pattern based analysis. To form a distinct Kikuchi pattern from each grain, the electron beam of the TEM must be focused to a small spot, e.g., 2 μm diameter or less. At small electron beam spot sizes hydrocarbon contamination rapidly builds up. The backpolishing procedure does not necessarily polish the portion of a tip covered by these hydrocarbons. And because the electron beam of the TEM polymerizes the hydrocarbons, solvents do not remove them. To overcome this problem, a contaminated specimen is placed in a Plasmod (March Instruments Incorporated, Concord, California) for 2–3 min. A Plasmod generates an oxygen plasma in a quartz chamber that consists of oxygen free radicals that react with hydrocarbons to produce water vapor, carbon monoxide, and carbon dioxide that are pumped out of the chamber. Not all alloys need to be placed in a Plasmod for cleaning, e.g., W and W (Re) are backpolished in a solution that removes hydrocarbon buildup. Nickel and its alloys, on the other hand, use a solution similar to that for iron and iron alloys (10% perchloric acid/90% 2-butoxyethanol) and so they also would need a Plasmod treatment. In a study of segregation to GBs in a Ni(C) alloy, a tip could not necessarily be backpolished after TEM analysis.

Figure 5 exhibits an example of how well the Plasmod removes hydrocarbon buildup. In Fig. 5(a) the arrows point to contaminated areas that were intentionally introduced along the length of this tip. This amount of contamination is in excess of what normally occurs during a TEM analysis. Next it was placed in the Plasmod for 2 min, and Fig. 5(b) shows that the hydrocarbon contamination has been completely removed. It is also demonstrated that the Plasmod treatment does not interfere with the ability to backpolish—see the examples in Sec. II D.

C. Tip geometry

The traditional specification of tip geometry employs the tip radius (r) and the shank angle (α). For the purpose of GB studies, however, it is more appropriate to use the GB-to-tip separation (GBTS) and the GB diam and its corresponding value of α. Figure 6 defines these parameters for the three possible GB geometries. The purpose of these definitions is to define the accessibility of a GB in a tip for APFIM analysis. The GBTS indicates how much material is field evaporated before a GB is in the FIM field-of-view. The GB diams indicate the range of voltages necessary to image and analyze a GB. For our research we are interested in the geometries in Fig. 6(a) or in Fig. 6(b) for GB diam I≈GB diam II, as we want to analyze the chemical composition in a direction perpendicular to a GB plane. We determined that for this type of tip geometry that the GBTS needs to be in the range 30–200 nm, and the GB diam needs to be between 40 and 80 nm for α≤20°; for our APFIM this range of GB diameters corresponds to FIM best image voltages of 5.5–9 kVdc at tip temperatures of 35–45 K, and uncorrected gauge pressures of 2×10⁻⁷.
FIG. 4. (a)–(h) represent an example of backpolishing of an Fe-3.0 at. % Si alloy specimen with a GB perpendicular to the tip axis. This type of GB orientation is important in our GB segregation studies because data deconvolution is not necessary when the GB chemical composition is measured in a direction perpendicular to a GB plane. Underneath each micrograph are the total elapsed electropolishing time, the number of pulses applied, the duration of each pulse, and the rate of removal of material along the length of the tip.

$2 \times 10^{-5}$ Torr Ne. Although determined for selected tip geometries, these specifications have applicability to all geometries.

These tip geometry specifications were empirically determined based on our procedure to maximize the probability of GB identification, and subsequent APFIM analysis when a specimen is placed in the APFIM. If a tip meets the tip geometry specifications, then the following procedure works best: (1) Use dc and pulsed-field evaporation to develop the endform of the top grain enough to see a pattern of poles. Make note of the grain orientation relative to a fiducial mark. The poles are easiest to Index when there are five 110 poles and two 200 poles in the field-of-view; the image is, in general, quite disordered atomically, but the 110 and 200 poles are always discernible. The Fe-3 at. % Si specimens have a (110) drawing texture and, therefore, one 110 pole always resides at the center of an FIM image; (2) continue to remove the top grain by field evaporation until the GB appears in the field-of-view, and at this point the GB usually passes through one or more of the 110 and 200 poles on the periphery of an FIM image; (3) field evaporate away the top grain continuously until the GB appears as a complete circle; (4) align the probe hole parallel to the GB, in which case the probe hole periphery is concentric with the image of the GB; and (5) perform APFIM. Figure 7 shows a field evaporation sequence of an Fe-3 at. % Si tip. Note the prominence of the 110 and 200 poles relative to the others. In Fig. 7(d), the top grain has been field evaporated away enough so that the GB appears as a complete circle. Drawing a pole diagram of the top grain aids in the process of tracking the GB position as it is removed by the pulsed-field evaporation process. An additional aid in tracking the GB position is to lower the imaging voltage below the best image voltage. At this lower voltage the image of a GB appears as a wide dark band. This technique is not, however, completely reliable because dark bands occur in an image of a single crystal as a result of local variations of the radius of curvature of a tip.

This procedure may fail for GBTs $< 30$ nm, because a tip must be field evaporated to a smooth and spherical final endform to see a distinct pattern of poles, and for distances $< 30$ nm it is not always possible to obtain a final

![Diagram](attachment:diagram.png)

FIG. 5. An example of the utility of using a Plasmod to remove hydrocarbon contamination from an Fe(Si) sample. (a) A tip on which hydrocarbon contamination was intentionally introduced in the TEM. (b) The same tip as in (a), but after placing the contaminated tip in a Plasmod for 2 min.

![Diagram](attachment:diagram.png)

FIG. 6. Schematic diagrams illustrating the definitions of the GB-to-tip separation (GBTS), GB diam, and shank angle ($\alpha$) for the three possible orientations of a GB relative to a tip axis. Since $\alpha$ usually varies along the length of a tip it is measured at the same place where the GB diam is measured. There is an optimum range for the tip parameters to guarantee the observation and subsequent APFIM analysis of a GB. In (c) a GBTS is not defined because the GB plane extends to the surface of the tip.
FIG. 7. A field evaporation sequence of an FIM image showing a GB image changing its position as the top grain is removed by the field evaporation process. Identifying a GB in an Fe-3 at. % Si specimen is easy if the tip diam is at least 40 nm, so that four 110 and two 200 poles appear on the periphery of an image. The GB position is most discernible when it passes through one or more of these low-index poles. The usefulness of these poles is because they consist of more concentric rings and cover more of the tip surface than do other poles.

endform without removing the GB by the field-evaporation process. For GBTSs > 200 nm the process of field evaporating the top grain to expose both the GB and the bottom grain takes an inordinate amount of time. The GB diam is important because for GB diameters <40 nm, the four 110 and two 200 poles on the periphery of an image are not necessarily visible before the GB is reached. The upper limit of 80 nm for the GB diam is determined by the fact that we want the voltages applied to a tip during imaging and atom probe analysis to be <11 kVdc. For the Fe-3 at. % Si alloy studied Si embrittles GBs, and it was found necessary to use a total voltage <11 kVdc to avoid excessive failure rates due to fracture that is most likely nucleated at GBs that are oriented at ~45° to the tip axis; the hydrostatic pressure on a tip is approximately constant, but the larger the tip radius the greater is the probability of there being more than one GB subjected to a high shear stress. Other nucleation sites for fracture are defects on the shank of a tip introduced during backpolishing.

The lower limit specification of the GB diam decreases as α increases because the field-of-view of a tip increases with α. We have, however, only examined a few specimens with a shank angle greater than 20°, as our sample preparation procedure allows us to systematically produce tips with low values of α. After tip sharpening in the zone electropolisher α is typically in the range 3°–10° and the taper on a shank is very uniform; our criterion during zone polishing for determining when a tip has a low value of α is optical transparency of the tip region under 200x magnification. The process of backpolishing typically increases α to the range 7°–20°.

The upper limit specification for the GB diam value varies because the necessary imaging voltage depends on α according to the relation $E = V/kr$, where $E$ is the best image electric field for neon, $V$ is the applied dc voltage, $r$ is the tip radius, and $k$ is a parameter that takes into account the nonspherical shape of a tip and is a function of α. An empirical equation for $k$ is given by

$$k = 0.59 (\alpha/2)^{1/3} \left(x/r\right)^{0.13},$$

where $x$ is the tip-to-channel plate distance; note well, that as α increases the value of $k$ increases. Figure 8 is a plot of the relation GB diam = $2r = (2/kE)V$ for $k=4$–10 and for $E=35$ V nm$^{-1}$. Superimposed on this plot are experimental data points for tips in which a GB was observed in the APFIM. Because most tips are not symmetrical in cross section this experimental data does not necessarily obey the property that as α increases $k$ increases. Figure 8 is still, however, useful and it indicates that as long as a GB diam is <80 nm and α is less than ~20°, that the voltage necessary to image a GB is <11 kVdc. However, for α >20° the upper limit specification for the GB diam becomes ~60 nm.

The most important tip geometry parameters are the GB diam and the value of α; together they determine the
FIM image field-of-view and the required image voltage. This observation is important because the backpolishing procedure does not control the relative sizes of the tip geometry parameters. Our backpolishing procedure, therefore, focuses solely on achieving a GB diam within specifications. Most tips are asymmetrical in cross-section and the largest dimension determines the minimum voltage necessary to image a tip. It is, therefore, important to measure this asymmetry and to keep the largest GB diam within the specifications. As already discussed, by the nature of the tip sharpening and backpolishing procedure \( \alpha \) is almost always below 20°. But if the final value is greater than 20°, then the data in Fig. 8 tell us that the GB diam specification is reduced to between 40 and 60 nm instead of 40–80 nm. The experimental data of Fig. 8 are also useful for situations where a GBTS exceeds 200 nm. For example, if the data indicate that a GB first begins to image at \( >6 \) kV because the tip diam at this point is 50 nm and \( \alpha \approx 10° \), then the top grain is quickly removed by the field-evaporation process and the possibility of detecting this GB does not exist until an image voltage close to 6 kV is reached. No compensating procedure exists for when the GBTS is less than 30 nm. If the backpolishing produces a tip with a very smooth and spherical surface, then the GBTS can be negligibly small—a good FIM image is produced after field evaporating just a few atomic layers. The backpolishing procedure cannot, however, be used to control the quality of the surface of a tip.

D. Examples

Figure 9 exhibits five different specimens that were successfully analyzed via TEM and APFIM. Each row of micrographs is of one sample that passed through all stages of an experiment. In column A are micrographs of GBs before TEM analysis. After TEM analysis, but before backpolishing, the specimens were placed in the Plasmod for 2 min to remove the hydrocarbon contamination. In column B are micrographs of the same specimens as in column A after the backpolishing procedure. Each tip has a geometry satisfying the requirements specified in Sec. II C. Specimen No. 1 has a GBTS exceeding 200 nm, but as explained in Sec. II C locating this GB in the APFIM only takes more time than for the other specimens. Each specimen was then placed in our APFIM. The micrographs in column C are of the tips in column B, after the APFIM analyses of the GB chemical compositions was completed. Underneath each micrograph in columns B and C are the FIM operating conditions used to image the tips, respectively.

The micrographs in Fig. 9 demonstrate how successful we are at systematically and reproducibly preparing specimens containing GBs when we perform the sample preparation in a batch mode; that is, when we process many specimens in parallel, not moving to the next step in the procedure until all the specimens have passed through the same step. To obtain these five specimens we began with a batch of ten. One failure was due to a tip fracturing during plasma cleaning. A second tip failed because the GB was removed accidently during backpolishing. The remaining
TABLE I. An example of a step-by-step procedure for preparing specimens. To increase the probability to 100% that the preparation is successful, the specimen is backpolished both before and after TEM analysis. The initial backpolishing is stopped when the tip dimensions are satisfactory for forming Kikuchi patterns from the two grains. The values of GB diam and GBTS are determined with the specimen in the TEM by comparing the tip to fiducial marks on the TEM phosphor screen. \( \Delta d/\Delta t \) is the time rate of change of GBTS.

<table>
<thead>
<tr>
<th>Step No.</th>
<th>Comments</th>
<th>GB diam (nm)</th>
<th>GBTS (nm)</th>
<th>Pulse width (ms)</th>
<th>Number of pulses</th>
<th>( \Delta d/\Delta t ) (nm ms(^{-1}))</th>
<th>Pulse Voltage (V)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>After sharpening a tip, a GB is located 17.1 ( \mu )m from the tip and the GB diam is 1.1 ( \mu )m.</td>
<td>1157</td>
<td>17140</td>
<td>1157</td>
<td>17140</td>
<td>100</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>2.</td>
<td>Begin an initial backpolishing of the tip to bring the tip geometry to approximately 0.2–0.5 ( \mu )m for the GB diam and about 3 ( \mu )m for the GBTS. Apply a 100-ms-wide pulse to the tip.</td>
<td>694</td>
<td>9434</td>
<td>100</td>
<td>1</td>
<td>24</td>
<td>12</td>
<td>270</td>
</tr>
<tr>
<td>3.</td>
<td>After applying the 100-ms pulse, GB diam= 9.3 ( \mu )m and GBTS=14.3 ( \mu )m.</td>
<td>556</td>
<td>3676</td>
<td>60</td>
<td>1</td>
<td>18</td>
<td>12</td>
<td>270.2</td>
</tr>
<tr>
<td>4.</td>
<td>Perform GB Kikuchi pattern analysis.</td>
<td>408</td>
<td>2451</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Put the tip in the Plasmod for 3 min to remove the hydrocarbon contamination.</td>
<td>327</td>
<td>1564</td>
<td>40</td>
<td>1</td>
<td>15</td>
<td>12</td>
<td>270.5</td>
</tr>
<tr>
<td>6.</td>
<td>Begin the final backpolishing to bring the GB into the tip region for APFIM analysis.</td>
<td>197</td>
<td>985</td>
<td>20</td>
<td>1</td>
<td>14</td>
<td>12</td>
<td>270.6</td>
</tr>
<tr>
<td>7.</td>
<td></td>
<td>148</td>
<td>640</td>
<td>16</td>
<td>1</td>
<td>17</td>
<td>12</td>
<td>270.5</td>
</tr>
<tr>
<td>8.</td>
<td></td>
<td>128</td>
<td>394</td>
<td>12</td>
<td>1</td>
<td>15</td>
<td>12</td>
<td>270.5</td>
</tr>
<tr>
<td>9.</td>
<td></td>
<td>99</td>
<td>197</td>
<td>6</td>
<td>1</td>
<td>16</td>
<td>12</td>
<td>270.7</td>
</tr>
<tr>
<td>10.</td>
<td></td>
<td>69</td>
<td>128</td>
<td>3</td>
<td>1</td>
<td>12</td>
<td>11</td>
<td>269.3</td>
</tr>
<tr>
<td>11.</td>
<td></td>
<td>64</td>
<td>108</td>
<td></td>
<td></td>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

three failed because the tips became contaminated during backpolishing. The overall success rate is 50% for the preparation and GB identification procedures described in this paper. The primary source of failure is the contamination of a specimen as it is being backpolished.

To overcome this contamination problem and so increase the success rate toward 100%, we find it necessary to work with one specimen at a time and to complete the sample preparation procedure within 3–8 h. We also find it important to adhere to a specimen preparation procedure similar to the one listed in Table I. For this procedure, we backpolish immediately after we sharpen a tip and after TEM analysis. We find this two-step backpolishing procedure necessary because a tip is susceptible to becoming contaminated at distances far from a tip, and this susceptibility is exacerbated by prolonging the time between sharpening a tip and backpolishing. We, therefore, reduce the dimensions of a tip to as small a value as possible before TEM analysis, without interfering with our ability to perform an accurate Kikuchi pattern analyses. The best Kikuchi patterns are formed when the GB diam is approximately 0.180–0.460 \( \mu \)m and when the GBTS is no less than 2 \( \mu \)m—during this initial backpolishing we can check the quality of the Kikuchi patterns in between backpolishing steps. The backpolishing procedure is started with wide pulses, because there is a dependence on the width of a polishing pulse and the maximum diam that can be polished without a specimen becoming contaminated; a pulse 10-ms wide has a higher probability of contaminating a portion of a tip of 1-\( \mu \)m diameter than does a pulse of 100-ms duration. Note from the table that at pulse widths \(<3 ms the applied voltage is reduced to 11 Vdc and the temperature of the solution is reduced to 269.5 K to prevent the formation of small pits.

III. QUANTITATIVE ATOM-PROBE FIELD-ION MICROSCOPY

Alloy concentrations measured via APFIM are a function of the following APFIM operating conditions: (1) pulse fraction \( f \)—the ratio of the pulse voltage \( V_p \) to the steady-state imaging voltage \( V_{de} \); (2) specimen temperature \( T \); (3) average field evaporation rate—average number of ions evaporated per field evaporation pulse; (4) crystallographic direction analyzed; (5) physical area on the specimen tip subtended by the probe hole; (6) pulse
over the range of specimen temperatures used. The data were recorded of&-defined as the ratio of the pulse voltage ($V_p$) to the steady-state evaporation rate of 0.01. Near a 110 pole at a pulse frequency of 60 Hz and an average field diameter (<7 nm). The crystallographic direction analyzed effect can be minimized by using a low average field-evaporation rate.

The experiments to determine the APFIM operating conditions to accurately measure the Si concentration in an Fe-3 at. % Si specimen were performed on a straight time-of-flight mass spectrometer. The procedure to determine the optimum APFIM operating conditions was to measure the concentration of silicon as a function of $f$ in the range 5%–25% for $T = 35–55$ K. All $T$s were stable to within ±0.5 K, and all the data were recorded with the probe hole covering a region near a 110 pole. The probe hole-tip separation was maintained such that the nearest 110 pole—if covered by the probe hole so that the probe hole periphery was concentric with the pole rings—has no more than two or three rings enclosed by the probe hole. The evaporation rate was maintained at <0.01 and the pulse repetition rate was 60 Hz; we used a large pulse frequency to eliminate the effect of a low pulse repetition rate on the measured concentration. The results are plotted in Fig. 10—Si concentration (at. %) versus $f$—where as $f$ decreases from 25%, the amount of scatter in the Si concentration increases as does its average value for the temperature range employed. This increase in Si concentration with decreasing $f$ is a result of Fe being selectively field evaporated, so that the apparent Si concentration increases; the observed evaporation field of pure Si is 38 V nm$^{-1}$ and for pure Fe it is 35 V nm$^{-1}$ (Ref. 27)—therefore, to first-order Fe is preferentially field evaporated. From Fig. 10 we conclude that $T$ can be as high as 55 K, as long as the value of $f$ is at least 15%. Because of the experimental scatter at $f = 15\%$, 20%, or 25%, an approximate error bar of ±0.4 at. % can be attached to the mean bulk composition, and this yields a bulk concentration of 2.5 ± 0.4 at. % Si.

An independent measurement of the bulk Si concentration was made by Ledoux & Company (Teananck, New Jersey). They used gravimetric analysis to obtain a value of 2.7 ± 0.39 at. % Si; this is based on the ASTM procedure for determining silicon concentrations. The Ledoux & Company value is in close agreement with the atom probe results exhibited in Fig. 10.

IV. AN EXAMPLE OF THE COMBINED USE OF TEM AND APFIM ON THE SAME BOUNDARY

A. Experimental procedure

The following is a step-by-step procedure for a typical experimental study of GB segregation: (1) anneal 185-μm-diam by 1.0-cm-long Fe-3.0 at. % Si wires at 823 K for 68 h in a static 99.999 at. % pure argon atmosphere to induce Si segregation at GBs; (2) electropolish a tip so that the tip is electron transparent; (3) using TEM identify a GB in a tip to be analyzed by both TEM and APFIM; (4) electropolish to bring the GB diam in the range 0.180–0.460 μm and the GBTS to approximately 4 μm; (5) analyze the GB crystallography via TEM; (6) place the tip in a Plasmad for 2–3 min; (7) electrolytically backpolish to bring the GB close to the tip and ensure that the final tip geometry is optimal for observing the GB and analyzing its chemical composition via APFIM; and (8) place the tip in the APFIM, locate the GB, and determine its chemical composition.

B. Results and discussion

1. Specimen preparation

Figure 11(a) exhibits a TEM micrograph of a GB near the tip of an Fe-3.0 at. % Si wire that was backpolished to produce a tip with the requisite geometry to locate a GB and analyze it via APFIM. Indicated are the dimensions of the GB diam (69 nm) and the GBTS (108 nm). The GB was imaged at voltages in the range 7.0–7.2 kV at $T = 35$ K, and a gauge pressure of $3 \times 10^{-6}$ Torr Ne. Figure 11(b) shows an FIM micrograph of the same tip. The GB appears as a circle; the projection of the probe hole diameter at the FIM image is 6.3 nm.

2. TEM analysis

The results of the TEM analysis show that the GB misorientation is described by $c = [0.684, 0.728, 0.043]$ and $\theta = 62.280\degree$; the normals to the GB in the two grains are
FIG. 11. (a) An example of a tip that was backpolished to bring a GB into the tip region for subsequent APFIM analysis. This tip has the proper GB geometry for its observation and analysis in an atom probe; the GBTS is 108 nm and the GB diam is 69 nm. In (b) the intersection of the GB plane with the tip is delineated with a dotted circle and the probe hole, with a 6.3-nm diam, is centered on the top grain for a compositional analysis.

3. APFIM analysis

Figure 12 displays an integral profile from this tip, recorded with the GB plane parallel to the plane of the probe hole as depicted in Fig. 11(b). The data were recorded with $f = 15\%$ and $T = 35 \, K$, and the measured GB concentration is $10.0 \pm 3.0 \, \%$ Si. The Si concentrations on the sides immediately adjacent to the GB are $3.0 \pm 0.77$ and $2.7 \pm 0.43 \, \%$ Si. Therefore the average segregation enhancement factor for Si is $3.51 \pm 0.34$ at 823 K, for a GB with the structure given in the preceding section. This average value was determined by first averaging the bulk concentrations on each side of the GB and then dividing this average into the GB concentration. The error was determined by propagation of the original errors.

ACKNOWLEDGMENTS

This research is supported by National Science Foundation Grant No. DMR-8819074 (Dr. B. MacDonald, grant officer). It also utilized central facilities of the NSF-funded Materials Research Center.