The FIM, TEM, k-y-k, autocorrelation, and AP L data sets all indicate a continuous increase in the scale of the microstructure with aging time. The SANS data, however, all contain a distinct statistically significant discontinuity after aging for 24 h. The mean size of the chromium-enriched phase, Ti, measured from the AP composition profile also has this discontinuity occurring approximately the same time as the error associated with these measurements is larger. This discontinuity in size has been previously observed by RPFIM in this alloy at higher aging temperatures [2]. The time at which the discontinuity occurs corresponds to the time at which the phases attain a steady state condition with respect to composition and volume fraction. For the very early aging times the width of the interface region between the phases is slightly more extended than for the longer aging times. The Xe and AP thickness measurements are in general agreement for the "size" of the chromium-enriched regions. The SANS 2/3 measurements which give a measure of the periodicity of the microstructure fall between the size and periodicity categories.

The time exponent which is frequently used to compare experimental data to theoretical models shows some variation but is significantly less in all cases than the classical Lifshitz-Slyozov-Wagner value of 0.33. This experimental variation will make comparison with other theoretical models difficult.

V CONCLUSIONS

While the results are in general agreement, this study has shown that significant differences are measured by the three instruments in an evolving microstructure where there are many changes occurring simultaneously. The results also highlight the advantages of using a variety of techniques to fully characterize the scale and nature of a microstructure.

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REFERENCES


EFFECT OF FIELD-EVAPORATION RATE ON QUANTITATIVE ATOM-PROBE ANALYSIS

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Résumé - Les effets de la vitesse d'évaporation de champ sur l'analyse chimique quantitative des matériaux à l'aide d'un microscope à émission d'ion avec sonde atomique sont examinés. Des exemples de grandes valeurs erronées de la concentration de Ti dans les alliages Mo-10 at.% Ti et Mo-10 at. % Ti-1.0 at. % Zr (T2M) sont présentés et nous montrons que la cause est due à une grande vitesse d'évaporation de champ. Les arguments de base utilisés pour expliquer ces observations peuvent être appliqués pour la quantification de tous les systèmes d'alliages étudiés à l'aide de la technique du microscope à émissions d'ion avec sonde atomique.

Abstract - The effects of field-evaporation rate on the quantitative chemical analysis of materials by atom-probe field-ion microscopy are considered. Examples of erroneously high measured values of the Ti concentration in Mo-1.0 at. % Ti and Mo-1.0 at. % Ti-0.08 at. % Zr (T2M) alloys are presented and the cause is shown to have been due to a high field-evaporation rate. The basic arguments used to explain these observations are applicable for the quantitation of all alloy systems studied by the atom-probe field-ion microscopy technique.

I - INTRODUCTION

The quantitation of chemical analysis by the atom-probe field-ion microscope (FIM) technique is an important and basic problem. Earlier work by Wagner/1/ found that the titanium concentration in a Mo-1.0 at. % Ti alloy is a very sensitive function of the absolute number of atoms detected per field-evaporation pulse; i.e., the instantaneous field-evaporation rate (FEB). Also Watts and Ralph/2/ have demonstrated that the Ti composition of Ni-12.0 at. % Ti alloy is a function of the pulse fraction (F). Miller and Smith/3/ have investigated the effects of fundamental experimental parameters on the measured composition of an Fe-3.0 at. % Si transformer steel. Yamamoto and Seidman/4,5/ and Herschitz and Seidman/6/ have conducted an extensive investigation of the effects of a number of experimental parameters on the compositions of the ordered alloys PtCo and Ni3Mo, and CuNi and CoFe alloys, respectively.
In this paper we consider the effect of FER on the quantitative chemical analysis of materials by atom-probe FIM. Examples of erroneously high measured values of the titanium concentration in Ho-1.0 at.%Ti and Ho-1.0 at.%Ti-0.08 at.%Zr (ZrM) alloys are presented and the cause is shown to have been due to to high FER. The motivation for this work was a study of the mechanism(s) for radiation-induced swelling in these alloys. Although only examples from these two alloy systems are presented, the basic argument are applicable to the quantitative analysis of all alloy systems studied by the atom-probe FIM technique.

II - SOME BASIC CONCEPTS

During a typical atom-probe analysis, high-voltage pulses are applied repeatedly to a specimen until one or more atoms are field evaporated in the form of positively charged ions. The ions are then rapidly accelerated to their terminal velocities with the smallest mass-to-charge (m/n) ratio ions achieving the highest terminal velocities. The ions then travel down a flight tube approximately 2.2 meters in length to a chevron channel electron multiplier array (CEMA) detector which senses the arrival of each ion at the detector/7. If several ions are field-evaporated simultaneously by the application of a single field-evaporation pulse and if each of the ions has a different (m/n) values, then each ion will be detected and an exact quantitative chemical analysis will be obtained. However, if several ions with the same (m/n) value field-evaporate simultaneously, they will all arrive at the detector at the same instant in time, and hence only one signal from the chevron CEMA will be produced. This signal(1) will then be interpreted erroneously as the arrival of a single ion and will result in a false determination of the chemical composition or isotopic distribution in the case of a pure material. In general, the evaporation of more than one atom per field-evaporation pulse always results in the measured composition indicating a higher concentration than was actually present in the material of the least abundant species. And correspondingly a lower measured concentration of the most abundant species.

A specific example is presented to illustrate the point made in the previous paragraph. Consider a material which contains two species(2)-A and B. Let \( C_a \) and \( C_b \) equal the concentrations of species A and B, respectively. In the case of the different charge states or isotopes, the concentration of each species is simply determined by the relative population of each species after field evaporation. Assume that exactly two atoms field evaporate for each evaporation event. Then there are three possible field-evaporation products-two A atoms, two B atoms, or one A atom and one B atom. If one A and one B atom evaporate then they are both detected. However, if two A atoms or two B atoms evaporate then they are detected as one A or one B atom, respectively. The probability of formation for each evaporation product is as follows:

<table>
<thead>
<tr>
<th>Evaporation Product</th>
<th>Probability</th>
<th>Number of Atoms Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A</td>
<td>( C_a^2 )</td>
<td>1A</td>
</tr>
<tr>
<td>2B</td>
<td>( C_b^2 )</td>
<td>1B</td>
</tr>
<tr>
<td>1A + 1B</td>
<td>( 2C_aC_b )</td>
<td>1A + 1B</td>
</tr>
</tbody>
</table>

Note that the sum of the individual probabilities is \( (C_a^2 + C_b^2 + C_aC_b) \) as is required. After \( N \) evaporation events--\( 2N \) total atoms evaporated--the number of A atoms detected is equal to \( NC_a^2 + 2C_aC_b \), the number of B atoms detected is equal to \( NC_b^2 + 2C_aC_b \), and the total number of atoms detected is equal to \( N(1 + 2C_aC_b) \). Note well that the total number of atoms detected is less than the number field evaporated (2N). The measured concentrations of A and B, \( C_a^* \) and \( C_b^* \), respectively, are given by:

\[
C_a^* = \frac{(C_a^2 + 2C_aC_b)/(1 + 2C_aC_b)}{1}
\]

\[
C_b^* = \frac{(C_b^2 + 2C_aC_b)/(1 + 2C_aC_b)}{1}
\]

Therefore the ratio of Eqn. (1a) to Eqn. (1b) is given by:

\[
\frac{C_a^*}{C_b^*} = \frac{(C_a^2 + 2C_aC_b)/(C_b^2 + 2C_aC_b)}{1}
\]

Now if \( C_a^* < C_b^* \) then we have the following inequality:

\[
(C_a^*/C_b^*) > (C_a/C_b)
\]

Thus the measured concentration of solute \( C_a^* \) is greater than the actual concentration of solute \( C_a \). For a dilute alloy of B in A--\( C_a^* \approx C_b^* \)--the measured concentration of B approaches twice the actual concentration. That is, \( C_a^* \) approaches \( 2C_b^* \) and a 100% error results.

It is also important to note that the number of atoms detected is significantly less than the number field evaporated. The ratio \( B \) of atoms detected to atoms field-evaporated is given by the expression:

\[
B = (0.5 + C_aC_b)
\]

(1) The assumption has been made that a detector pulse-height analysis has not been performed, if the output pulse height is proportional to the number of ions striking the detector simultaneously, an exact quantitative analysis can be obtained even if several ions had field-evaporated simultaneously. No evidence presently exists demonstrating a proportionality between pulse height and number of incident ions. In fact, evidence does exist (Ref. 9) which indicates a very broad pulse-height distribution resulting from a single incident ion. This strongly suggests that establishing an accurate and useful proportionality between number of incident ions and detector pulse height would be extremely difficult.

(2) The term species is used here in a general sense to indicate any atom which field evaporates with a unique (m/n) value. This can include chemically different atoms which have different (m/n) values or chemically identical atoms which have different (m/n) values; e.g. different isotopes of the same element or a single isotope which field evaporates in several charge states or both.
The range of $B$ in Eqn. (4) is $0.5 \pm 0.75$. For a multispecies system in which two atoms field evaporate simultaneously, the measured concentration of component $i$ ($C_i$) is given by the equation:

$$C_i = \frac{C_i^0 + 2C_i^1}{1 + C_i^2}.$$

(5)

For the more general expression [Eqn.(5)] the value of $B$ is given by the expression:

$$B = 0.5(1 + \frac{C_i^0}{C_i^2}).$$

(6)

The range of $B$ in Eqn.(6) is $0.5 \pm 0.5 + (S-1)/2S$, where $S$ is the number of species.

The above discussion assumed that the number of species field evaporating during each field evaporation event is less than the maximum number of time-of-flights (TOFs) which can be measured with the digital timer—eight in our case/10/. If more than eight species are field evaporated per pulse then only the first eight species which strike the detector are analyzed. This biases the chemical analysis towards the smallest values and thus the measured concentrations of the smallest (m/n) values are greater than the actual concentrations. This is an instrumentation problem and is not a fundamental limitation of the technique, since it can be avoided by constructing a digital timer with a sufficient number of timing chains. For example, Sakurai et al./11/ employ a digital timer with 16 timing chains.

The above paragraph describes two distinctly different mechanisms which can result in an inaccurate quantitative chemical analysis. The common feature of both mechanisms is that the errors in the chemical analysis increase as the FER increases.

III - EXPERIMENTAL RESULTS AND DISCUSSION

An integral profile showing the spatial distribution of Ti in a Mo-10 at.% Ti alloy is presented in Fig 1. The analysis was performed with the specimen at 35 K, with $T=0.10$ from a region near the (110) pole. Two local fluctuations in the Ti integral profile which exhibit very large local concentrations of Ti are indicated (A and B in Fig 1). Figure 2 exhibits the corresponding rate of field evaporation during the atom-probe analysis in the form of a graph of the number of Mo ions detected per field-evaporation event, averaged over approximately 100 atoms, versus the cumulative number of Mo atoms (or depth). Note that both the A and B fluctuations in the Ti concentration are directly correlated with high local field-evaporation rates. However, Fig. 3 also shows that fluctuation A in the Ti concentration exhibited in Fig 1 is also associated with a large local increase in the carbon concentration. Three other integral profiles were recorded on this Mo-10 at.% Ti alloy and no carbon was detected/1,12/. The decomposition of CO on the surface of the FIM specimen would result in a carbon and an oxygen profile, with CO appearing at the same (m/n) value as the major Ti isotope ('$^{48}$Ti*). It is possible that fluctuation A—which is near the surface—in the Ti profile (Fig 1) is actually due to oxygen and is not associated with a high field FER. In the case of fluctuation B on carbon was detected and, hence, the large Ti concentration can only be attributed to a high local FER. A detailed analysis of the FER revealed that seven of the nine Ti atoms contained in fluctuation B were detected in three consecutive evaporation events in which a total of eight atoms per field evaporation event were detected. Since a maximum of eight species per field evaporation event can be detected employing our digital timer/10/, considerably more than eight atoms probably field evaporated per field evaporation event. This high FER caused the erroneously large measured Ti concentration via the two mechanisms discussed in Section II. For both fluctuations the high local FERs were caused by the application of excessively high voltages to the specimen. This was determined by monitoring both the rate of increase of the specimen voltage and the evaporation efficiency—defined as the number of atoms detected per field-evaporation pulse. The voltage on the specimen was increased rapidly with a resultant increase in the evaporation efficiency and thus the FER. The overall average evaporation efficiency was $0.05$ atoms per pulse versus an average efficiency of greater than 1 atom per pulse near fluctuations A and B. In the region away from these local fluctuations the average Ti concentration was $0.35 \pm 0.08$ at.% Ti—which is in good agreement with our other measurements on this alloy/1,12/.

![Composition Profile of Ti in an unirradiated Mo-10 at.% Ti alloy.](image1)

![Evaporation Rate Profile of Mo-10 at.% Ti.](image2)

There are two possible explanations why the value—$0.35 \pm 0.08$ at.% Ti—is less than the nominal concentration of 0.90 at.% Ti supplied by the manufacturer. First, Ti may have also field evaporated in the +2 charge state and would therefore have been superimposed...
directly on the Mo\textsuperscript{+4} portion of the (m/n) spectrum. Thus, all of the doubly charged Ti would be indistinguishable from the much more abundant Mo\textsuperscript{+4}. Second, an alternate explanation is that the remaining Ti was not in solid solution. Considerable evidence exists which shows that TiC precipitates can form in both Mo-1.0 at.% Ti and TiZr13. These precipitates are large and at a low number density on the scale of an FIM observation. And, hence, the probability of detecting any Ti contained within a TiC precipitate is extremely small. In the course of developing a successful specimen preparation technique for the Mo-1.0 at.% Ti alloy, extensive transmission electron microscope examinations of the electropolished FIM specimens were made. Occasionally large precipitates (\(100\ \text{nm}\) diam.) were observed; presumably they were TiC precipitates. This clearly indicated that precipitates were present in the material used in this experiment. Since the manufacturer's value of the Ti concentration included the Ti contained in precipitates, there must have been less than 0.9 at.% Ti in solid solution. Obviously the Ti concentration measured by the atom-probe technique represents a lower limit to the amount of Ti in solid solution. This argument is also consistent with the experimental observation that no carbon was detected; this shows that the vast majority of the carbon was not in solid solution and that it may reside completely in the TiC precipitates/13/.

Another example of a high FER causing an erroneously high measured Ti concentration occurred in examining the (111) plane of the same Mo-1.0 at.% Ti alloy specimen. In this case the average measured Ti concentration was 2.1 at.% Ti. The measured Ti concentration versus FER is exhibited in Fig. 4 and tabulated in Table I. Note that as the FER increases the measured Ti concentration increases rapidly. For example, when eight atoms were detected per field-evaporation event the average measured Ti concentration is approximately 19.7 at.% Ti. In this case several hundred Mo-Ti atoms must have been field evaporated in order to yield a measured Ti concentration of 19.7 at.% Ti versus the nominal 1.0 at.% Ti. This erroneously large measured Ti concentration is attributed to
both of the mechanisms discussed in Section II. Since over one-half of the total Ti atoms detected from the (111) plane are associated with an FER corresponding to eight atoms per evaporation event (see Table I), the overall measured Ti concentration is erroneously high. By way of comparison Fig. 5 shows the measured Ti concentration versus FER for the TZM alloy. Note that the same general tendency for the measured Ti concentration to increase with FER is observed. However, the overall measured Ti concentration is not significantly influenced by high evaporation rates—that is, 6.7 or 8 atoms detected per evaporation event—since only a small fraction of the total number of Ti atoms detected were associated with high evaporation rates (see Table 2). An important observation during the analysis of the (111) plane of the TZM alloy is that the average evaporation efficiency is less than 0.1 atom per pulse. This is comparable to the evaporation efficiency employed in all of the other atom probe analyses of this material from the vicinity of the (110) plane, which yielded quite satisfactory evaporation rates and hence reasonably accurate quantitative measurements of the Ti concentration. Thus the large FER is the result of the intrinsic mode of field evaporation of the Mo (111) plane/14,15/ and was not due to the application of an excessively high voltage to the APFIM specimen. A visual observation of the evaporation of the (111) plane of Mo confirmed this conclusion. It was observed that the field evaporation of atoms from the (111) plane of Mo is highly nonuniform. The repeated application of field-evaporation pulses resulted in little or no field evaporation, until suddenly with the application of only a few additional pulses an entire plane of atoms was removed. It is this intrinsic mode of field evaporation of the (111) plane of Mo which caused the high FER in spite of the low evaporation efficiency employed. Thus, the (111) plane and in general any nonuniformly field evaporating region of any material, may not be suitable for quantitative atom probe analysis.

IV - CONCLUSIONS

Although we have only presented experimental results for two Mo-based alloys (Mo-1.0 at.% Ti and Mo-10 at.% Ti-0.08 at.% Zr, (TZM) alloy, the following conclusions which are applicable in general to all alloy systems were reached.

(1) - The field-evaporation rate—defined as the number of atoms detected per evaporation event—has a strong influence on the accuracy of an atom probe analysis. As the FER increases, the measured concentration of the less abundant species increases and in general, when more than one atom field evaporates per pulse the measured concentration of the less abundant species is greater than the actual concentration.

(2) - For very high FERs in which the number of species field evaporating exceeds the number of TOF events which can be measured, the measured concentration of the smallest (m/n) value species is greater than its actual concentration, i.e., the analysis is biased toward the lowest (m/n) values.

(3) - The FER was not always related to evaporation efficiency. In the case of a nonuniformly field evaporating plane—e.g., the (111) plane of molybdenum—very high FER was observed although small evaporation efficiencies were employed. Thus nonuniformly field evaporating regions of a specimen may be intrinsically unsuited for quantitative atom-probe analysis.

(4) - Local fluctuations in the composition indicated in an integral profile may be artifacts induced by a high local FER.

(5) - The ability to measure a large number of TOF events is a distinct advantage in atom-probe FIM since

(a) The FER and its effect on quantitative atom-probe analysis can be

Table 2 - The measured titanium concentration as a function of evaporation rate for a Mo-1.0 at.% Ti-0.08 at.% Zr (TZM) alloy.

| EVAPORATION RATE | NUMBER OF ATOMS | TITANIUM CONCENTRATION | TITANIUM ATOMIC%
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Number of atoms detected per evaporation event)</td>
<td>Mo²</td>
<td>Mo³</td>
<td>Mo⁴</td>
</tr>
<tr>
<td>1</td>
<td>858</td>
<td>3422</td>
<td>131</td>
</tr>
<tr>
<td>2</td>
<td>464</td>
<td>2193</td>
<td>153</td>
</tr>
<tr>
<td>3</td>
<td>219</td>
<td>1162</td>
<td>126</td>
</tr>
<tr>
<td>4</td>
<td>151</td>
<td>688</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>122</td>
<td>397</td>
<td>53</td>
</tr>
<tr>
<td>6</td>
<td>157</td>
<td>187</td>
<td>29</td>
</tr>
<tr>
<td>7</td>
<td>45</td>
<td>125</td>
<td>29</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
<td>108</td>
<td>27</td>
</tr>
</tbody>
</table>

*The ± values were calculated from ±N/ZN values where N is the number of atoms detected.
REFERENCES

The references are not clearly visible in the image. They are likely to be a list of scientific works cited in the text, possibly including authors, titles, and publication details. This information is crucial for understanding the sources and contributions of the research discussed in the text. If you need specific details from the references, please provide the full text of the document, and I will be happy to extract the relevant information for you.