In the present study the clear resolution of three peaks is due to the particular crystal structure; no surface semi-channels exist in the (011) directions of Mg(0001) while the atomic chain spacing is quite large. This is not the case, for example, in the (211) directions on the same surface (see inserts in figs. 1a and 2a). Estimation of the time spent near the surface shows that QS scattered ions typically spend \(2.9 \times 10^{-14}\) s within a \(1.5\) a \((-0.040\) nm) of the surface, QD scattered ions spend \(3.0 \times 10^{-14}\) s and ZZ scattered ions spend \(3.3 \times 10^{-14}\) s.

The implication is drawn that, for the \(Ar^+\)/Mg system, no dramatic change in neutralization efficiency occurs, within the above variations of time.

In systems where there are distinct QS, QD and ZZ peaks (such as that described) systematic investigation of relative peak height against primary ion energy \(E_p\) may give direct information on neutralization lifetimes.

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References


THE QUANTITATIVE COMPOSITIONAL ANALYSIS AND FIELD-EVAPORATION BEHAVIOR OF ORDERED Ni,Mo ON AN ATOMIC PLANE-BY-PLANE BASIS: AN ATOM-PROBE FIELD-ION MICROSCOPE STUDY

Masahiko YAMAMOTO ** and David N. SEIDMAN
Department of Materials Science and Engineering and the Materials Science Center, Bird Hall, Cornell University, Ithaca, New York 14853-0121, USA

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Atom-probe field-ion microscope analyses were performed on specimens of ordered Ni,Mo. The (211) fundamental and (101) superlattice planes, of the body-centered tetragonal lattice, were analyzed chemically on an atomic plane-by-plane basis. It was demonstrated that the composition of each individual plane can be determined as a function of depth without any ambiguity. The overall coverage Mo concentration was measured to be 17.1 at% for the (211) fundamental plane as compared to 19.4 at% Mo by conventional chemical techniques. Possible sources of this discrepancy are discussed. The details of the field evaporation behavior of the (211) fundamental and (101) superlattice planes were studied. The field evaporation behavior is described in terms of the field evaporation rate, the order of the field evaporated ions, etc. Each individual atomic plane field-evaporated on an atomic plane-by-plane basis for the (211) fundamental plane. While the (101) superlattice plane a group of planes consisting of one plane of Mo atoms and four planes of Ni atoms field-evaporated as a unit. An abnormal increase in the number of Mo atoms was found in the central portion of the (211) fundamental plane. Possible mechanisms for the abnormal field evaporation rate are discussed. Finally, it is concluded that the atom probe technique can be used, in this complicated ordered structure, to follow: (1) the physics and chemistry of the field evaporation process; and (2) the chemistry of the alloy as a function of position, on a subnanometer scale, throughout the specimen.

I. Introduction

The determination of the composition of an alloy on an atomic plane-by-plane basis by the atom-probe field-ion microscope (FIM) technique hereinafter called an atom probe has proved itself to be a convenient and useful method for the measurement of composition with a depth resolution of 0.1 to 0.3 nm (1-3 Å) [1-3]. When one uses this method it is not necessary to

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** On leave-of-absence from the Department of Materials Science and Engineering, Osaka University, Suita, Osaka 565, Japan.
observe continuously the FIM image in order to detect the complete field-evaporation behavior of an individual atomic plane. Furthermore, when the atom probe is controlled by a minicomputer it is possible to determine the composition of each field-evaporated plane on an on-line basis. The method is illustrated schematically in fig. 1 [11]. In this paper we apply this method to the analysis of full-ordered Ni$_4$Mo.

Ordered Ni$_4$Mo has one of the most complex crystal structures (body-centered tetragonal) [4] of all the ordered alloys and intermetallic compounds which have been studied by the FIM technique. Although a number of studies of the order–disorder transformation and related topics on the Ni$_4$Mo alloy have been made [5–18], the details of the field-evaporation behavior of this alloy have not been investigated.

The purpose of the present study is to demonstrate the results of chemical analyses, on an atomic plane-by-plane basis, for the (211) fundamental and (101) superlattice planes of the body-centered tetragonal (bct) lattice. And to clarify the field-evaporation behavior of ordered Ni$_4$Mo. Our observations demonstrate that a complicated field-evaporation process— as well as the chemistry— can be followed as a function of both depth and atomic configuration in the plane.

2. Experimental details and procedures

The Ni$_4$Mo specimens used for our studies had a composition of 80.6 at% Ni and 19.4 at% Mo; the chemical analyses were performed by the Chemical Analytical Facility of the Cornell Materials Science Center. Specimens in the form of wires (0.254 mm diam.) were heat treated to obtain a highly ordered state in the following way [15]: They were initially annealed at 800°C for two days. Next the specimen temperature was gradually decreased over a period of two weeks to 600°C, and finally the specimen was cooled to room temperature during the course of one day. FIM specimens were then prepared by electropolishing the wires in a concentrated hydrochloric acid solution. All of the experiments were performed employing an atom probe which has been described previously in detail [19,20].

In our experiments the fundamental and superlattice planes of the bct lattice were chemically analyzed, in detail, on an atomic plane-by-plane basis. The analyses were performed by rotating the FIM specimen so that the normal to the plane analyzed was in the center of the probe hole [1]. The background pressure in the atom probe was in the low 10$^{-10}$ Torr range and the specimen was at 60 K during each analysis. The pulse fraction (f) is given by the ratio $V_{\text{pulse}}/V_{\text{dc}}$; where $V_{\text{pulse}}$ and $V_{\text{dc}}$ are the pulse and steady-state voltages, respectively. The value of f used was 0.10 and the pulse frequency was constant at a value of 60 Hz. In the bct structure of ordered Ni$_4$Mo every plane can be classified as being either a fundamental or superlattice plane. The chemistry of the specific planes considered in the present work are exhibited in fig. 2. In the

* In this paper we consider only the (211) fundamental and (101) superlattice planes; hence, from now on we will not use the Miller indices in discussing these planes.
case of the fundamental plane every atomic layer has the stoichiometric composition: 80 at% Ni and 20 at% Mo - see fig. 2a. While in the case of the superlattice plane the first plane consists of solely Mo atoms and the subsequent four planes solely of Ni atoms - see fig. 2b.

3. Results

3.1. General features of the spectrum of ordered Ni₄Mo

Fig. 3 is a mass spectrum of the fundamental plane. It consists of H⁺, Ni²⁺, Mo³⁺ and Mo⁵⁺ peaks. The charge states of Ni and Mo in the mass spectra for the (200) and (101) superlattice planes of ordered Ni₄Mo are the same as the ones for the fundamental plane. Figs. 4 and 5 show the details of the Mo⁵⁺, Ni²⁺ and Mo³⁺ peaks. In all of the spectra of Ni₄Mo the Ni²⁺ portion of each spectrum overlaps with the Mo⁵⁺ isotopes; however, the peaks associated with the five naturally occurring isotopes of Ni (⁵⁸Ni, ⁶⁰Ni, ⁶⁴Ni,

Fig. 3. A mass spectrum of ordered Ni₄Mo analyzed in the (211) fundamental plane region. The data were recorded with the specimen at 60 K and a pulse frequency of 60 Hz was employed for the pulse field-evaporation disssection process. The spectrum consists of Ni²⁺, Mo³⁺ and Mo⁵⁺ peaks and a peak of H⁺ from the residual hydrogen in the atom probe.

Fig. 4. The Mo⁵⁺ portion of the mass spectrum exhibited in fig. 2. The seven naturally occurring isotopes of Mo are readily distinguished.

Fig. 5. The Ni²⁺ and Mo³⁺ portion of the mass spectrum exhibited in fig. 2. The isotopes of Ni and Mo are labeled and the exponential decay behavior of ⁵⁸Ni²⁺, ⁶₀Ni²⁺ and ⁶⁴Ni²⁺ is indicated by the sloping lines.


The seven naturally occurring isotopes of Mo, (92Mo, 94Mo, 95Mo, 96Mo, 97Mo, 98Mo, 100Mo) are readily distinguished from one another in the regions containing Ni2+ and Mo3+, or Mo2+. However, 64Ni cannot be distinguished from 58Ni. (The 64Ni isotope was neglected in determining the composition of the alloy, as its isotopic abundance is only 0.904%.)

It is seen that the 58Ni, 60Ni and 62Ni peaks are asymmetrical in shape and decrease exponentially on the high mass-to-charge ratio side. This exponential decay is a result of the energy-deficit effect [21,22]. It is assumed that the peaks on the high mass-to-charge side obey the exponential expression

\[ N = N_0 \exp(-\alpha^{-1} [(M/n)_{\text{obs}} - (M/n)_{\text{max}}]) \]

where \( N \) is the number of events observed, \( (M/n)_{\text{max}} \) corresponds to the mass-to-charge ratio at which the maximum in the peak height occurs, \( N_0 \) is the number of events at \( (M/n)_{\text{max}} \), \( (M/n)_{\text{obs}} \) is the observed value and \( \alpha \) is a characteristic decay constant. Eq. (1) can be recast in the form

\[ (M/n)_{\text{obs}} = (M/n)_{\text{max}} - \alpha \ln(N/N_0) \]

and the value of \( \alpha \) extracted from the experimental peaks. For the 58Ni2+, 60Ni2+ and 62Ni2+ peaks the value of \( \alpha \) is 0.15 [in units of \( (M/n) \)].

The region consisting of solely the Ni2+ isotopes is denoted A (58Ni2+, 60Ni2+ and 62Ni2+). Region B consists of 92Mo3+ and 62Ni2+ and region C is composed of the isotopes 94Mo3+, 96Mo3+, 98Mo3+, 99Mo3+ and 100Mo3+. The seven naturally occurring isotopes of Mo, that evaporated in the 2+ charge state, are referred to as region D. The number of ions detected in each of these regions is summarized in Table 1. The uncertainty of the composition, caused by the overlapping of the tails of the peaks, was less than \( \pm 0.5 \) at% Mo. The average composition obtained was 17.1 at% Mo and this value is less than the chemical composition of 19.4 at% Mo.

12. The composition and the field evaporation behavior of the fundamental plane

Fig. 6 displays the field evaporation behavior for the fundamental plane. Each of the three graphs in Fig. 6 consists of a plot of the cumulative number of the specified species versus the cumulative number of field-evaporation pulses. The latter quantity is proportional to both time and depth. Each step in

**Table 1**

Analysis of ordered Ni-Mo by atom-probe FIM

<table>
<thead>
<tr>
<th>Ion</th>
<th>Region</th>
<th>Number of atoms</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni2+</td>
<td>A</td>
<td>2886</td>
<td>82.9 at% Ni</td>
</tr>
<tr>
<td>Ni2+</td>
<td>B</td>
<td>217 (103)</td>
<td>82.9 at% Ni</td>
</tr>
<tr>
<td>Mo3+</td>
<td>C</td>
<td>349</td>
<td>17.1 at% Mo</td>
</tr>
<tr>
<td>Mo2+</td>
<td>D</td>
<td>154</td>
<td>17.1 at% Mo</td>
</tr>
</tbody>
</table>

Total of regions A, B, C and D: 3606

*In addition to the numbers given for the Ni and Mo events there were 155 other events, most of which were Ni1+.*

*This was deconvoluted into the Ni2+ and Mo3+ contributions employing the chemical alloy composition and the natural abundances of 62Ni2+ and 92Mo3+.*
these figures corresponds to the field-evaporation of a fundamental plane.

The procedure used to generate the data of fig. 6 is illustrated schematically in fig. 1. First the crystal plane is placed under the probe hole and the magnification adjusted. Then \( V_p \) is added to \( V_{dc} \) at a frequency of 60 Hz. In stage I the atoms which field-evaporate from the kink or ledge sites of the top plane (1) do not go through the probe hole. As the diameter of the top plane (1) shrinks the field-evaporated ions pass through the probe hole and are detected - stage II of fig. 1a. When all the atoms in the top plane (1) have been field evaporated the process repeats itself for the next plane (2) - see stage III. This field-evaporation behavior is displayed in a plot of the cumulative number of atoms as a function of the cumulative number of field-evaporation pulses - fig. 1b. Thus one step in this plot corresponds to the field-evaporation of one atomic plane. This means that the analyses exhibited in fig. 6 have a depth resolution of 0.208 nm (2.08 A) - that is, the (211) interplanar spacing.

In order to obtain a clear step-like field-evaporation behavior for ordered Ni-Mo the following three parameters must be carefully controlled: (i) the field-evaporation rate; (ii) the specimen temperature; and (iii) the relative size of the probed area to the maximum size of the top plane. When the field-evaporation rate is too high the steps are not detected and the plot increases almost monotonically. On the other hand when the field-evaporation rate is very low it is also difficult to obtain a clear step-like behavior. Furthermore, a specimen temperature of < 60 K is necessary to obtain a step-like field-evaporation behavior. At a temperature of > 100 K the field-evaporation rate became very large and we continuously detected pulse field-evaporated atoms. With the magnification adjusted such that the probed area was less than the maximum size of the top plane we obtained a well-defined step-like field-evaporation behavior. Alternatively, when the area probed was greater than the maximum size of the top plane, the atoms in the next plane can be simultaneously detected. Hence, the correspondence of one step to one atomic plane is not satisfied. The above three parameters are interrelated - therefore, they must be adjusted, in an iterative fashion, to obtain well-defined step-like behavior.

The average values of the quantities \( N_{layer}/N_{pulse} \) and \( N_{ion}/N_{pulse} \) for the run of fig. 6 were \( 9.1 \times 10^{-3} \) layers pulse\(^{-1} \) and \( 1.0 \times 10^{-2} \) ions pulse\(^{-1} \); where \( N_{layer} \), \( N_{ion} \) and \( N_{pulse} \) are the total number of atomic planes analyzed, the total number of ions detected and the total number of field-evaporation pulses, respectively. (These parameters are used to quantify the field-evaporation process, as they are easy parameters to measure. However, they may not be the most fundamental parameters in terms of understanding the phenomenon of field evaporation.) The quantities \( N_{layer}/N_{pulse} \) and \( N_{ion}/N_{pulse} \) for plane numbers 29 to 32 can be determined from fig. 6; they are \( 1.0 \times 10^{-4} \) layers pulse\(^{-1} \) and \( 1.3 \times 10^{-2} \) ions pulse\(^{-1} \). In a previous paper [23] we introduced the quantity \( N_{ion}/N_{pulse} \) as a parameter which is proportional to field-evaporation rate. Once the distance between the tip and the probe hole has been fixed, this parameter yields a relative field-evaporation rate. However, the quantity \( N_{layer}/N_{pulse} \) expresses the field-evaporation rate more definitely than the quantity \( N_{ion}/N_{pulse} \). This is because the quantity \( N_{layer}/N_{pulse} \) is independent of the size of the analyzed area while the quantity \( N_{ion}/N_{pulse} \) is dependent on the size of the analyzed area even when the field-evaporation rate is constant. (The quantities \( N_{layer}/N_{pulse} \) and \( N_{ion}/N_{pulse} \) should be called the field-evaporation rate and the ion-detection rate, respectively.) On the other hand, the quantity \( N_{ion}/N_{pulse} \) corresponds to the local slope in a plot of

![Fig. 7](image-url)

**Fig. 7.** The top most figure exhibits the Mo concentration as a function of plane numbers (25-32) - that is, depth - for the fundamental plane. The next figure shows the total number of atoms per plane as a function of plane number. The remaining three figures are similar to the previous one, except the quantities plotted on the ordinate scale are as follows: number of Ni atoms per plane in the A region, number of atoms (Ni + Mo) per plane in the B region and number of atoms (Mo) per plane in the C and D regions.
the cumulative number of atoms versus the cumulative number of field-evaporation pulses. And thus it is convenient as a measure of the relative field-evaporation rate at each point of the experimental curve. In this paper the quantity $N_{\text{tot}}/N_{\text{pulse}}$ is used in the above sense, even though it is not the absolute field-evaporation rate.

The average field-evaporation rate is approximately constant for plane numbers 29 to 32 in fig. 6. However, the field evaporation rate within a given plane is not constant. For example, in the case of the step for plane number 30 (fig. 6), the initial field-evaporation rate (periphery of the plane) is extremely small and the final field-evaporation rate (central portion of the plane) is very large. The same field-evaporation behavior is also true for all the other planes (1 to 32) in this sequence.

The chemistry of eight successive fundamental planes is presented in fig. 7.

![Graph of Ni$_4$Mo (211)$_{\text{act}}$ Fundamental Plane](image)

Fig. 8. The top figure is for the cumulative number of Ni atoms versus the cumulative number of Ni plus Mo atoms. The bottom figure is for the cumulative number of Mo atoms versus the same abscissa. Note the abnormal increase in the number of Mo atoms field evaporated from the central portion of each plane. Both figures are for the fundamental plane. All the data for these figures were taken from the same run as for fig. 6.

![Graph of Cumulative Number of Ni and Mo Atoms for (211)$_{\text{act}}$ Fundamental Plane](image)

Fig. 9. The cumulative number of Mo atoms versus the cumulative number of Ni atoms for the fundamental plane. Note that the first atoms field-evaporated are nickel and the last ones are molybdenum. All the data for this figure were taken from the same run as for fig. 6.

The top graph in fig. 7 reveals the Mo concentration for each of these eight fundamental planes as a function of plane number (depth). The minimum and maximum concentrations observed were 14.4 and 19.5 at%; the average concentration for these eight planes is 17.2 at% Mo. This value is almost the same as the average measured concentration (17.1 at% Mo) (table 1).

More details of the field evaporation behavior of the fundamental plane are seen in fig. 8; the plane numbers are indicated in the figure. Nickel atoms were detected continuously, during the dissection process, until the central portion was reached (top graph). In the central portion of each plane there was a deficiency of Ni atoms (top graph). The number of Mo atoms detected in the central portion of each plane (bottom graph) was abnormally high – that is, much greater than one would expect on the basis of the stoichiometry of the fundamental plane (see fig. 2).

The order of detection of the Ni and Mo atoms, for each of the planes, is exhibited in fig. 9. It is noted that the Ni atoms began to field evaporate before the Mo atoms and that the abnormal increase – discussed above – of Mo atoms in the central portion of each plane is evident.

### 1.3. The field evaporation behavior of the superlattice plane

Fig. 10 exhibits the field evaporation behavior of the superlattice plane. And fig. 11 shows plots of the cumulative number of Ni atoms (top graph) and Mo atoms (bottom graph) versus the cumulative number of Ni plus Mo atoms for
Fig. 10. The field-evaporation behavior of the fundamental plane. The topmost figure is a plot of the cumulative number of Ni plus Mo atoms versus the cumulative number of field-evaporation pulses. The middle and bottom figures are plots of the cumulative number of Ni or Mo atoms, respectively, versus the cumulative number of field-evaporation pulses. One step corresponds to a group of planes consisting of one plane of Mo atoms and four planes of Ni atoms.

Fig. 11. The top figure is a plot of the cumulative number of Ni atoms versus the cumulative number of Ni plus Mo atoms for the superlattice plane. The bottom figure is a plot of the cumulative number of Mo atoms versus the same abscissa.

regime seven of fig. 10. While fig. 12 shows a plot of the cumulative number of Mo atoms versus the cumulative number of Ni atoms for regimes seven and eight of fig. 10. Figs. 10, 11, and 12 for the superlattice plane correspond to figs. 6, 8, and 9 for the fundamental plane, respectively. However, each major step in fig. 10 for a superlattice plane corresponds to the removal of a group of
planes consisting of one plane of Mo atoms and four planes of Ni atoms (see fig. 2). For example, in fig. 10 the step labeled seven consists of these five planes. That this was the case can be seen from the center and bottom graphs in fig. 10 – compare the field-evaporation behavior towards the end of each step. The vertical parallel lines in fig. 10 help to demonstrate that the last plane to field evaporate, within each major step, consists solely of Ni atoms. It is noted that even for the field-evaporation of a unit group the initial field-evaporation rate (periphery of the plane) is small and final field-evaporation rate (central portion of the plane) is very large.

Fig. 11 shows that the field evaporation of the Ni atoms occurs almost continuously (top graph) while the Mo atoms field evaporate continuously in only the first four-fifths of the regime (sections a to d in the bottom graph) – and they do not field evaporate in the last one-fifth of regime 7 (section e in the bottom graph). Fig. 12 exhibits the order of detection of the Ni and Mo atoms in regimes 7 and 8. From an examination of fig. 12 it is clear that the first atoms to field evaporate were Mo and the last ones were Ni. After the first Mo atoms had been field evaporated a mixture of Ni plus Mo atoms were field evaporated. This behavior is denoted by the letters a, b, c and d (fig. 12) to stress the point that one plane of Mo atoms and three planes of Ni atoms were involved. It is emphasized that during the pulse dissection of these four planes Mo atoms from the topmost plane were still being field evaporated.

4. Discussion

4.1. The determination of composition on an atomic plane-by-plane basis

The information contained in figs. 6 and 7 demonstrates that composition can be successfully determined on an atomic plane-by-plane basis for the fundamental plane. It is emphasized that this determination can be made without observing the field-ion image during the analyses. The same technique has also been applied to the compound semiconductor GaP [24] and ordered Pt,Co [25]. An alternative method of analysis requires the calculation of the number of atoms belonging to the analyzed area employing a field-ion image. Or one can simply assume that the number of atoms is equal to the value which corresponds to one atomic plane. The former method requires a knowledge of the magnification at each stage of the analysis. However, the automatic atomic plane-by-plane analysis method [1] allows one to determine the composition without any ambiguity. In the case of the fundamental plane each one should contain 80 at% Ni: 20 at% Mo, if the alloy is perfectly stoichiometric and fully ordered (fig. 2); that is, if the Bragg-Williams long-range order parameter is exactly equal to unity everywhere in the specimen. In our case we should have observed an average value of 80.6 at% Ni: 19.4 at% Mo. However, the average Mo concentration is 2.3 at% less than expected value. Furthermore the composition for each atomic plane was different. This could have had its origin in the following possible sources: (1) the alloy may not have been fully ordered; (2) the value of \( f \) employed was too small; and (3) the temperature of the specimen was too high [23].

The possibility that the alloy was not fully ordered cannot be answered precisely, because we were unable to measure the Bragg-Williams long-range order parameter for this alloy by the FIM technique [15]. The reason for this is that only the Mo atoms give rise to a visible image; however, excellent FIM images were obtained and it is our opinion that the specimens were almost fully ordered [15].

The second and third possible sources of the discrepancy are suggested by our results on Pt,Co [23]. In this work it was shown that the measured Co concentration is a function of the temperature of the specimen and the value of \( f \) employed – that is, the value of \( V_{de}/V_{de} \). Our results on Pt,Co imply that the use of a larger value of \( f \) (at 0.15) and a lower specimen temperature (\( < 40 \) K) may bring the atom-probe measurements in closer agreement with the average value obtained by conventional chemical analyses. It is noted that the very detection of Ni atoms – which are invisible in the FIM image – indicates that they were not all selectively field evaporated at \( V_{de} \) from the fundamental plane.
4.2. The field-evaporation behavior of the fundamental plane

The data presented in figs. 6, 8 and 9 shed light on the field-evaporation behavior of the fundamental plane. Note that all of the fundamental planes in ordered Ni₃Mo have the stoichiometric composition - 80 at% Ni: 20 at% Mo (fig. 2). The following three features of the field-evaporation behavior were found for the fundamental plane: (1) the field evaporation rate within a plane was not a constant value for both the Mo and Ni atoms, although the average evaporation rate was constant, i.e., the field-evaporation rate became higher for both the Mo and Ni atoms in the central portion of the plane; (2) the Ni atoms began to field evaporate before the Mo atoms; and (3) an abnormal increase in the number of Mo atoms in the central portion of each plane occurred.

Feature (1) has already been observed for pure metals - for example, for tungsten [2]. In this paper we have shown how rapidly both the Ni and Mo atoms field evaporate from the central portion of the plane. The rapid increase in the field-evaporation rate of the last remaining atoms in the central portion of a plane is due to an increase in the local electric field above individual atoms as the size of a plane shrinks. Feature (2) can be explained in terms of the difference in the evaporation fields of nickel and molybdenum. The evaporation fields of pure Ni and Mo are 3.6 and 4.5 V Å⁻¹, respectively [26]. Although the values of the evaporation fields for both elements should be different for the alloy, the relative values of the fields should be similar. Fig. 13 exhibits the topmost fundamental plane. Both Mo and Ni atoms can be retained within the indicated annular ring. The outermost circle passes through four Mo atoms situated at kink sites. The reason for this is that the evaporation field of Mo atoms from these kink sites is greater than for Ni atoms at kink sites. When the top atomic plane is at maximum size, Ni atoms at kink sites (e.g. atom A in fig. 13) field evaporate more easily than Mo atoms at kink sites (e.g. atom B in fig. 13). Therefore, the Ni atoms field evaporate before the Mo atoms when they are at kink sites. And after a certain fraction of the Ni atoms have been field-evaporated, the Mo atoms then begin to field evaporate, because Mo atoms at kink sites have a smaller coordination number than Ni atoms at ledge sites (e.g. atom C in fig. 13) the evaporation fields for Ni and Mo atoms may be identical or be inverted with respect to values for the ledge sites - it is a difficult problem to calculate these evaporation fields exactly. Hence, subsequent field-evaporation is a mixture of Ni atoms from ledge sites and Mo atoms from kink sites. When the top plane achieves a small diameter, all the remaining atoms are able to field evaporate, so that a complicated field-evaporation behavior can occur. This latter point is related to feature (3).

Miller and Smith [27] have reported that abnormal field-evaporation behavior occurred in the central portion of the (110) plane of an iron-3 wt% silicon alloy; that is, the silicon concentration was much greater in the central portion of the plane. Their observation is similar to the abnormal increase of Mo atoms in the central portion of the plane. Hence, to obtain the correct composition of an alloy, it is better to avoid taking data solely from the central portions of the plane.

3. The field-evaporation behavior of the superlattice plane

The results presented in figs. 10, 11 and 12 demonstrate that the field-evaporation behavior of the superlattice plane is considerably more complex than that of the fundamental plane. We had expected the superlattice plane to field evaporate on atomic plane-by-plane basis. However, a group of planes consisting of one plane of Mo atoms and four planes of Ni atoms field-evaporated as a unit. This is because the top plane is very stable, while the following three Ni planes are unstable and the last Ni plane is metastable. In order to explain the stability of the field-evaporating atoms let us consider the situation of atomic binding in the (101) superlattice plane. If atomic species and the slight distortion that occurs on ordering are ignored, then the ordered Ni₃Mo structure is fcc - therefore the atomic configuration can be considered in the basis of an fcc lattice. An atom in the first (101) plane, which corresponds to a (315) plane of the fcc lattice, does not have any first nearest-neighbor atoms in the same plane. The smallest distance between two atoms in the first plane corresponds to the third nearest-neighbor distance (4.42 Å). On the other hand, an atom in the first plane has two first-nearest-neighbor atoms in the second plane and two first-nearest-neighbor atoms in the third plane. Such an atomic arrangement implies that an atom in the first plane is bound more tightly by the underlying atoms than by the atoms in the
same plane—hence, the field-evaporating atoms are strongly influenced by the underlying atoms. In an ordered alloy the binding of the different species of atoms is stronger than that of the same species. Hence, Mo atoms in the first plane are bound tightly by Ni atoms in the second plane and Ni atoms in the fifth plane are also bound tightly by Mo atoms in the sixth plane. Thus the present field evaporation behavior of the superlattice plane can be qualitatively understood in terms of the binding of field evaporating atoms in each individual plane.

Recently, so-called spinodal ordering has been discussed as a mechanism for ordering in Ni rich Ni-Mo alloys, including Ni₄Mo [28]. It is a problem connected with periodic compositional fluctuations along certain crystallographic directions. To understand the details of spinodal ordering on an atomic scale the present type of atom-probe analyses, at various ordering stages, should give useful information.

5. Summary

(1) Atom-probe analyses were performed on specimens of fully-ordered Ni₄Mo.

(2) The (211) fundamental and (101) superlattice planes of the body-centered tetragonal (bct) lattice were successfully analysed chemically on an atomic plane-by-plane basis.

(3) In order to obtain an analysis based on an individual atomic plane it is necessary to obtain a well-defined step-like field-evaporation behavior.

(4) It was determined that the step-like field-evaporation behavior depends sensitively on the following three parameters: (i) the field-evaporation rate; (ii) the specimen temperature; and (iii) the relative size of the probed area to the maximum size of the top plane.

(5) The overall average Mo concentration was 17.1 at% for the fundamental plane— as compared to 19.4 at% Mo for the composition determined by conventional analytical chemistry techniques. The minimum and maximum concentrations for eight successive atomic planes of the fundamental plane were 14.4 and 19.5 at%.

(6) Possible sources of the discrepancy between the value measured by the atom probe technique and the value determined by conventional chemical analytical techniques may lie with the use of a smaller value of the pulse fraction (f) and a higher specimen temperature than the optimum experimental values. However, the detection of Ni atoms clearly indicates that they are not all selectively field evaporated at Fp; from the fundamental plane for a f of 0.10 and a specimen temperature of 60 K.

(7) The field-evaporation behavior of both the fundamental and superlattice planes were studied in detail.

(8) The field-evaporation rate accelerates in the central portion of the plane (or a group of the planes) for both the fundamental and superlattice planes. This is due to the increase in local electric field above individual atoms as the size of a plane shrinks.

(9) For the fundamental plane each individual atomic plane field evaporates on an atomic plane-by-plane basis.

(10) For the superlattice planes the characteristic step-like field evaporation behavior is due to the partial field evaporation of a plane of Mo atoms followed by the continued field evaporation of this Mo plane, intermixed with the field evaporation of the following three planes of Ni atoms. Finally, a plane of Ni atoms was found to field evaporate by itself.

(11) An abnormal increase in the number of Mo atoms in the central portion of the fundamental plane was detected.

(12) From the results and discussion presented in this paper it is our conclusion that the atom probe technique can be used, in this complicated ordered structure, to follow: (1) the physics and chemistry of the field evaporation process; and (2) the composition of the alloy as a function of position, on a subnanometer scale, throughout the specimen.

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References

PARTIAL DISORDER AND LEED DIAGRAMS

I. The S/Pt(110) system

V. MAURICE
Laboratoire de Physico-Chimie des Surfaces, ERA 315, Université Pierre et Marie Curie, ENSCP, 11 Rue Pierre et Marie Curie, F-75252 Paris Cedex 05, France

and

J. LEGENDRE and M. HUBER
Laboratoire de Physico-Chimie et Structures des Solides Impairs, LA 302, Université Pierre et Marie Curie, ENSCP, 11 Rue Pierre et Marie Curie, F-75252 Paris Cedex 05, France

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The LEED diagram observed for S/Pt(110) in the 4/12-5/12 coverage range shows a small incidence unit mesh with some zero intensity spots. It can be interpreted by partial disorder and asymmetry modulations. Two different methods of investigation have been used to get a structure model. The major part of this model is made of ordered structural elements of the configurations corresponding to the lower and higher concentrations and belonging to a single premonodisperse phase. The remaining part is made of atoms belonging to the other phases which are ordered with respect to the predominant region. A unique system of modulations is obeyed in 

Introduction

The S/Pt(110) system has been investigated by Berthier et al. using LEED techniques [1]. Their main results are schematically shown in fig. 1: several different LEED diagrams have been observed, all of which have small coincidence meshes. All the diagrams corresponding to a concentration on either side of the 4/12-5/12 region are normal diagrams with all expected spots observed complete diagrams) and they are consistent with high symmetry ordered structures: they are fundamentally different from the unique and almost constant patterns observed for S/Cu(110) and S/Pd(110), for instance [2,3].

But in the 4/12 < \theta < 5/12 region, the LEED diagram shows three remarkable features:

1. Some spots are missing (incomplete diagram);
2. the two most intense spots are close to the centre of the reciprocal unit cell;
3. they do not have equal intensities.

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