REPLY TO COMMENT BY H. NUMAKURA: ON THE QUANTITATIVE ANALYSIS OF NANOMETER DIAMETER MgO PRECIPITATES VIA ATOM-PROBE FIELD-ION MICROSCOPY

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Introduction

This is a reply to a comment by H. Numakura (see previous article) on a paper we recently published in this journal, on an initial study of the atomic mechanisms of internal oxidation in the Cu(Mg) system, employing the atom-probe field-ion microscope (APFIM) technique [1]. Numakura suggests, among other things, that the detection efficiency of the chevron detector is considerably different for the three ion species Cu, Mg and O and, in particular, that there is an unusually low detection efficiency for O ions. Thus in this paper we report on a careful study of the experimental conditions necessary to measure correctly the oxygen concentration of nanometer diameter MgO precipitates in a Cu matrix. At the end of this paper we return to Numakura’s comment.

APFIM has been successfully used to perform quantitative studies of the local composition of materials on an atomic scale. The unique features of APFIM -- a nanometer scale probe diameter and no data deconvolution procedures for chemical analysis -- allow for a reasonably straightforward interpretation of experimental results. The atom probe technique has been applied, for example, to the study of precipitation [2-4], spinodal decomposition [5], solute-atom segregation at grain boundaries and surfaces [6-8], and the chemical sequence across metal/ceramic heterophase interfaces [9,10]. In particular, the atomic scale local variation of the composition near internal interfaces and surfaces has been widely investigated using APFIM, since the spatial resolution for chemical analysis in a direction normal to the surface of the specimen is equal to the interplanar spacing of the region of material being analyzed and this distance can be equal to a tenth of a nanometer, the lateral resolution in the surface can be as small as 0.2 to 0.5 nm. Quantitative analysis using APFIM requires a careful examination of the following experimental parameters because of the relative evaporation fields of the constituent elements: (a) specimen temperature; (b) pulse fraction (ratio of the pulse voltage, Vp, to the steady-state voltage, Vdc); (c) field-evaporation rate; (d) the crystallographic planes examined; and (e) the composition of the background vacuum [11-16]. Thus, the examination of a new material by APFIM requires that these experimental parameters be examined in detail prior to commencing the study of a physical problem. This is different from other spectroscopic analyses that require standard specimens and also, very often, complicated deconvolution procedures. Atom probe experiments are quite simple once the optimum experimental conditions are established. And it is well known that those experimental parameters may strongly affect the results of a quantitative analysis.

Recently, quantitative analyses of metal oxide precipitates and metal/metal-oxide interfaces have been performed using the atom-probe technique [9,10,17-20]. There are, however, no published systematic investigations of the above experimental parameters for metal oxides, even though there are several reports of off-stoichiometric metal-oxides. The physical properties of metal oxides are different from metals or semiconductors and, therefore, it is essential to understand how they behave in the high electric fields required for atom-probe analysis. In this paper we...
present the results of a detailed investigation of the above experimental parameters necessary for the investigation of nanometer diameter MgO precipitates in a completely internally oxidized Cu-1.86 at. % Mg alloy -- it is expected that the precipitates are close to stoichiometric. An important outcome of this investigation is that -- unexpectedly -- the pulse frequency in the range 10 to 60 Hz is an important variable in measuring the correct oxygen concentration in MgO precipitates.

Experimental Procedures and Experiments

An ingot with the composition Cu-1.86 at. % Mg was prepared via arc melting under a high purity argon atmosphere. This ingot was homogenized at 1273 K for seven days in an argon atmosphere. Its nominal composition after the anneal was obtained via the atomic absorption spectroscopy technique. Then the ingot was drawn into wire with a diameter of 200 μm. Next wires were internally oxidized for 2 h at 1223 K to form octahedral-shaped MgO precipitates, in a Cu matrix, using the Rhine's pack method [9,21]; this treatment produces a completely internally oxidized alloy. The experimental conditions necessary to control the diameter, the number density, and the morphology of the MgO precipitates are described in detail elsewhere [9].

Conventional transmission electron microscopy was used to measure the mean diameter and number density of MgO particles; a 200 kV Hitachi H700 microscope was used for this purpose, employing a double-tilt stage specially fabricated for observing FIM specimens in the form of 10 mm long wires [22]. Atom probe quantitation experiments were performed by varying the specimen temperature, pulse fraction (f) = Vp/Vdc, and pulse frequency at a fixed field-evaporation rate and at a background pressure of 3.7x10^{-8} Pa. The value of f= 0.1 and 0.15; the main constituents and their partial pressures in the background gas of the atom probe are H2 (1.7x10^{-8} Pa), H2O (4.6x10^{-9} Pa), CO (4.1x10^{-9} Pa), CO2 (1.79x10^{-9} Pa) and Ar (1.02x10^{-9} Pa). The partial pressures were measured using a UTI Model 100C residual gas analyzer.

Experimental Results and Discussion

Figure 1 exhibits a transmission electron micrograph of a completely internally oxidized Cu-1.86 at. % Mg FIM specimen used in the atom-probe quantitation experiments. The diameter of the MgO precipitates varies between 5 to 20 nm and the average number density of MgO precipitates is 2.6x10^{24} m^{-3}. This value for the number density of MgO precipitates is high enough that during the dissection of a specimen by the pulsed field-evaporation technique precipitates are intersected on a random basis -- this approach is called a random-area analysis; it is an intrinsically simpler approach than the one required to study individual grain boundaries [6,7,22]. A high resolution electron microscope study of the MgO precipitates has shown that they are octahedrally-shaped and faceted on (222) planes with a cube-on-cube orientation relationship with the Cu matrix; the precipitates are semi-coherent with the matrix as a result of the geometrically necessary misfit dislocations required to take up a misfit (τ) of 0.1483 between the two phases [9]; τ = 2(\text{a}_{\text{MgO}} - \text{a}_{\text{Cu}})/(\text{a}_{\text{MgO}} + \text{a}_{\text{Cu}}),\text{ where }\text{a}_{\text{i}}\text{ are the lattice parameters of MgO and Cu.}

Figure 2 shows the oxygen concentration of MgO precipitates as a function of pulse fraction (f = 0.1 and 0.15) and specimen temperature (30 to 60 K) at a fixed pulse frequency of 60 Hz. Each data point in Fig. 2 represents a composition measurement of one to three MgO precipitates, and the associated error bars represent plus or minus one standard deviation -- that is, the total length of each error bar is two standard deviations -- of a binomial distribution [21]. The field-evaporation rate during data collection was controlled by regulating the increment of the steady-state voltage (Vdc) and the pulse voltage (Vp) to try to maintain an average value of only 0.005 events pulse^{-1} at a fixed value of f; this evaporation rate is obtained via an algorithm in the APFIM operating system of the Macintosh IIfx computer that controls our atom probe [24]. This result indicates that the weighted mean concentration of the magnesium oxide precipitates is 50.0±1.0 at. % oxygen, and is independent of temperature in the range 30 to 60 K for values of f = 0.1 and 0.15; the ±1.03 at. % O is equal to the weighted standard deviation [25]. We note, however, that the initial field-evaporation rate is very high when an MgO precipitate is first uncovered at the surface of an FIM specimen. In many cases the number of ions collected per field-evaporation pulse was more than 10 and in some cases...
formed by completely internally oxidizing 200 was discovered that the measured oxygen concentration of were produced by a value of 60 Hz yields the correct stoichiometry over the temperature range 30 to 60 while at a specimen temperature of 50 K and f exceeded 128. We employ a new time-to-digital converter that has 128 channels [26] and this allows us, in order to avoid erroneous quantitation, to discard data when an excessive number of channels is filled. At this initial stage of uncovering an MgO precipitate at a specimen's surface, failure of the tip due to mechanical fracture was quite common. This is most likely due to the difference in the mechanical properties of the hard Cu matrix.

We also investigated the frequency dependence (10 to 60 Hz) of the oxygen concentration in MgO precipitates; thus the time between pulses ranged from 0.1 to 0.017 s. At low pulse frequencies (i.e., at 10 or 15 Hz) the number of events collected per field-evaporation pulse seldom exceeded 5 events pulse\textsuperscript{-1}, and catastrophic failure of an FIM specimens was infrequent. (The average number of events detected per field-evaporation pulse increased as the pulse frequency was increased, in spite of our efforts to maintain a fixed field-evaporation rate via computer control of V\textsubscript{p} and V\textsubscript{dc}. The electric field penetrates the MgO precipitates and the time for the charge to leak off an oxide precipitate is frequency dependent. Hence, the local electric field in an MgO precipitate is higher at higher pulse frequencies, and therefore the evaporation rate is higher.) Figure 3 exhibits the average oxygen concentration of MgO precipitates as a function of pulse frequency at a specimen temperature of 50 K and a pulse fraction of 0.1. Each data point in Fig. 3 represents a composition measurement of one to three MgO precipitates, and the associated error bars represent plus or minus one standard deviation -- the total length of each error bar is two standard deviations -- of a binomial distribution [23]. The results exhibited in this figure clearly demonstrate that the apparent mean concentration of an MgO precipitate is a strong function of the pulse frequency. (The only other published example of the effect of pulse frequency on concentration is for an Fe-3 wt. \% Si alloy [13]. The concentration of Si was correct (3 wt. \%) for a pulse frequency greater than only 1 Hz.) In the case of the MgO, however, the effect of the pulse frequency is a much stronger one and, clearly, preferential field-evaporation of oxygen between pulses must be responsible for the observed effect.

It is suggested that the preferential field evaporation of oxygen at V\textsubscript{dc} is due to the interaction of H\textsubscript{2} in the atom probe's background pressure to form H\textsubscript{2}O. This effect decreases with increasing pulse frequency as there is less and less time for the adsorbed H\textsubscript{2} to reach the individual MgO precipitates as they are dissected by the pulsed field-evaporation process. It is well known that hydrogen that is physisorbed on the shank of an FIM specimen -- that is covered with a chemisorbed layer of hydrogen -- can diffuse along the shank into the high-field region and react with atoms on the surface of an FIM tip [27], hydrogen chemisorbs on copper with a heat of adsorption of ~224 kJ mole\textsuperscript{-1} [28], and the shank of the FIM tip is, of course, pure copper. The reaction of H\textsubscript{2} with oxygen in an MgO precipitate yields H\textsubscript{2}O molecules, in the presence of a high electric field, and they are field desorbed in-between the field-evaporation pulses (V\textsubscript{p}) while the specimen is maintained at the steady-state voltage (V\textsubscript{dc}). Thus we could not detect H\textsubscript{2}O\textsubscript{m} molecules in the mass spectra.

Atom probe experiments on FeO [17], RuO\textsubscript{2} [18] and NiO [20] all exhibit hypochoiometric metal oxides, while an APFIM experiment on Rh\textsubscript{2}O\textsubscript{3} [19] measured the correct stoichiometry; the metal oxides in these experiments were produced by \textit{in situ} oxidation of elemental metal FIM tips. The effect of pulse frequency on the measured stoichiometry, described in this paper, may be quite general and hence it should be examined carefully when studying metal oxides via the atom probe technique. Also in view of these findings it is necessary to revisit the question of the atomic mechanism of internal oxidation of binary metal alloys using atom probe field-ion microscopy [1].

**Summary and Conclusions**

An APFIM study was performed on the effects of temperature (30 to 60 K), pulse fraction (f = 0.1 and 0.15), and pulse frequency (10 to 60 Hz) on the stoichiometry of MgO precipitates in a copper matrix; the precipitates were formed by completely internally oxidizing 200 µm diameter wires of a Cu-1.86 at.% Mg alloy at 1223 K for 2 h. It was discovered that the measured oxygen concentration of MgO precipitates depends on the pulse frequency, and that a value of 60 Hz yields the correct stoichiometry over the temperature range 30 to 60 K for either f = 0.1 or 0.15 -- see Fig. 2. While at a specimen temperature of 50 K and f = 0.1 the apparent concentration ranges from 15 to 50
at% O as the pulse frequency is increased from 10 to 60 Hz -- see Fig. 3. It is suggested that the hypostoichiometric oxygen concentrations result from the preferential field evaporation of oxygen, at the steady-state dc voltage, due to the reaction of H2 with oxygen in MgO precipitates to form H2O. This new finding implies that our initial experiments on the atomic mechanism of internal oxidation [1] must be repeated to take into account the effect of pulse frequency on stoichiometry. These experiments also rule out H. Numakura's suggestion that the observed oxygen deficiency is due to an unusually low Chevron detector efficiency for O ions.

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References

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FIG. 1. A transmission electron micrograph of a Cu field-ion microscope specimen containing a high number density of MgO precipitates. The precipitates exhibit classical Ashby-Brown or coffee-bean contrast effects. The wire axis is \langle111\rangle-type and therefore a set of \{222\}-type faces of the MgO precipitates is always perpendicular to the wire axis.

FIG. 2. The oxygen concentration of MgO precipitates as a function of pulse fraction \(f = 0.1\) and \(0.15\) and specimen temperature \((30\) to \(60\) K) at a constant pulse frequency of 60 Hz. The average field-evaporation rate was maintained at 0.005 events pulse\(^{-1}\) to prevent excessive evaporation during data collection. The error bars on each data point represents plus or minus one standard deviation for a total length of two standard deviations. The weighted mean oxygen concentration for all the measurements is \(50.01\pm1.03\) at\% O.
FIG. 3. The oxygen concentration of MgO precipitates obtained from atom-probe experiments as a function of pulse frequency (10 to 60 Hz) at a constant pulse fraction (f) equal to 0.1 and a specimen temperature of 50 K. The error bars on each data point represent plus or minus one standard deviation for a total length of two standard deviations. The results exhibited clearly indicate surprisingly that the apparent oxygen concentration of an MgO precipitate is a strong function of the pulse frequency.