



Comparison of the quantitative analysis performance between pulsed voltage atom probe and pulsed laser atom probe



J. Takahashi^{a,*}, K. Kawakami^a, D. Raabe^b

^aAdvanced Technology Research Laboratories, Nippon Steel & Sumitomo Metal Corporation, 20-1 Shintomi, Futtsu-city, Chiba 293-8511, Japan

^bMax-Planck Institut für Eisenforschung GmbH, Department for Microstructure Physics and Alloy Design, Max-Planck-Str. 1, 40237 Düsseldorf, Germany

ARTICLE INFO

Article history:

Received 1 April 2016

Revised 26 January 2017

Accepted 29 January 2017

Available online 31 January 2017

Keywords:

Atom probe

Quantitative analysis

Field evaporation

Preferential evaporation

Copper

ABSTRACT

The difference in quantitative analysis performance between the voltage-mode and laser-mode of a local electrode atom probe (LEAP3000X HR) was investigated using a Fe-Cu binary model alloy. Solute copper atoms in ferritic iron preferentially field evaporate because of their significantly lower evaporation field than the matrix iron, and thus, the apparent concentration of solute copper tends to be lower than the actual concentration. However, in voltage-mode, the apparent concentration was higher than the actual concentration at 40 K or less due to a detection loss of matrix iron, and the concentration decreased with increasing specimen temperature due to the preferential evaporation of solute copper. On the other hand, in laser-mode, the apparent concentration never exceeded the actual concentration, even at lower temperatures (20 K), and this mode showed better quantitative performance over a wide range of specimen temperatures. These results indicate that the pulsed laser atom probe prevents both detection loss and preferential evaporation under a wide range of measurement conditions.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Atom probe tomography (APT) is widely used in the fields of materials science and engineering because of its high performance in spatial resolution and detection limit for the quantitative analysis of the local composition in the materials. In pulsed voltage atom probe, single atoms on the tip surface are field evaporated by exposing them to a high surface electric field that is generated by the superimposition of a DC voltage (standing voltage) and a high pulsed voltage. On the other hand, in pulsed laser atom probe, single atoms on the tip surface are field evaporated by the application of DC voltage and pulsed laser radiation. The mechanism of the pulsed laser atom probe has been discussed, and the consensus view in conductive materials is obtained as the thermal effect where a near instantaneous rise in the temperature at the tip surface due to the pulsed laser radiation reduces the evaporation field of the material and triggers field evaporation of the surface atoms [1–4].

Degradation of the quantitative analysis performance has been reported in the analysis of solute alloying elements in steel depending on the analysis conditions [5–9]. For example, the apparent concentration of solute copper in ferritic iron tends to be lower than the actual concentration as the specimen temperature

increases, while the apparent concentration of solute silicon in ferritic iron tends to be higher than the actual concentration [5,6,8]. Such phenomena observed in pulsed voltage atom probe operation have been qualitatively interpreted by the mechanism based on “preferential evaporation or retention”, and recently, a corresponding model calculation for quantitatively understanding these effects has been reported [10]. However, when operating in pulsed laser atom probe, the influence of preferential evaporation or retention and other factors on the quantitative analysis performance are not yet sufficiently understood [11–13].

Presently, the pulsed laser atom probe is widely used for the atomic scale characterization of low conductive materials, such as oxide films and semiconductor devices [14–16]. In addition, it is also used for conductive materials, such as metals, because the yielding rate is significantly improved by preventing needle tip fracturing [17]. However, the quantitative analysis performance of the pulsed laser atom probe has not yet been sufficiently investigated in comparison with the pulsed voltage atom probe [18].

In this study, we investigated the quantitative analysis performance obtained from the voltage-mode and laser-mode of the LEAP3000XHR instrument under various specimen temperatures and laser pulse energy values using a Fe-Cu binary model alloy. The analysis of solute copper in steel is very sensitive to the measurement conditions because the evaporation field of solute copper is much different from that of the matrix iron [6,19]. We clarify the cause of deviations in the apparent concentration compared to the

* Corresponding author.

E-mail address: takahashi.3ctjun@jp.nssmc.com (J. Takahashi).

actual concentration and discuss the differences in the quantitative analysis performance between voltage-mode and laser-mode in terms of preferential evaporation.

2. Experiments

A binary model alloy, Fe–0.1Mn–1.35Cu (at.%), was used in this study. The copper content in the alloy was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Since copper easily precipitates as particles in ferritic iron in the temperature range between 400 and 700 °C, the Fe–Cu alloy was quenched in water after homogeneously annealing at 850 °C for 8 h in the ferritic phase [20]. The alloy was composed of a single, ferritic phase, and copper atoms were homogeneously distributed in solid solution. Small rods 0.3 mm × 0.3 mm × 10 mm in size were mechanically cut from the alloy, and needle-shaped specimens with a sharp tip were produced by the standard two-stage electropolishing method [2].

APT analyses were performed using an energy-compensated local electrode atom probe with a large-angle reflectron (LEAP3000X HR, Cameca). The instrument had a position-sensitive detector consisting of micro-channel plates (MCP) and the crossed helical delay-lines, and the flight pass through the reflectron was about 382 mm. A 532 nm wavelength green pulsed-laser with a 250 kHz pulse frequency was used for the laser-mode, and a pulsed voltage supplier with a 200 kHz pulse frequency was used for the voltage-mode. Various conditions were applied in this study (specimen base temperature: 20–100 K, laser pulse energy: 0.3–0.9 nJ). The atomic data sets were analyzed using the commercial software IVAS (version 3.6, Cameca) [21].

Recently, it has been reported that the delay-line LEAP detector has a detection loss of ions in the analysis of carbides, nitrides, semiconductors, or steels [12,13,22–25]. The detection loss of Fe²⁺ in steels depended on the measurement conditions, which was identified by a deviation of the apparent isotopic ratio of Fe²⁺ from the actual isotopic ratio [23]. If two ions with the same mass and charge are simultaneously field evaporated by the same pulse, the two ions hit the detector at almost the same time. And if the two ions hit the near positions on the detector, some of them are not detected because the two ions cannot be counted individually. ⁵⁶Fe²⁺ is the main isotopic ion of the matrix, and thus, the probability of detection loss is the highest. The detection loss of ⁵⁶Fe²⁺ hence results in an increase in the apparent concentration of alloying elements in the steel [23].

To accurately examine the influence of the measurement conditions on the apparent concentration of the alloying elements, the continuous analysis of the same specimen tip was conducted in the same analysis direction while the temperature and laser pulse energy were changed [8]. The detection rate was fixed at 0.5% ions/pulse on average, and was maintained constant throughout each measurement. It should be noted that the evaporation rate was actually changed because the tip radius was increased even if the detection rate was constant. However the preferential evaporation was not significantly influenced by the evaporation rate [10]. The number of ions collected exceeded 2 million for each measurement condition for the purpose of statistical reliability, with the standard error estimated to be less than 0.008 at.% for a solute copper concentration of 1.35 at.%.

In the mass spectra of APT analysis, the peaks at 27, 28, 28.5, and 29 Da were assigned to Fe²⁺, the peak at 27.5 Da was assigned to Mn²⁺, the peaks at 63 and 65 Da were assigned to Cu⁺, and the peaks at 31.5 and 32.5 Da were assigned to Cu²⁺. The absence of peaks at 32 and 64 Da indicate that no dimer ions of copper (Cu₂⁺ and Cu₂²⁺) were generated.

It should be noted that the tail of each peak in laser-mode is included within the mass range of the peak because the tail is

caused by real ions which field evaporate slightly late due to thermal conductivity.

3. Experimental results

Fig. 1(a) and 1(b) reveal the specimen temperature dependence of the apparent concentration (at.%) of solute copper measured in voltage-mode and laser-mode, respectively. The arrows in the figures indicate the actual concentration of solute copper. The measurement in voltage-mode was conducted with a pulse frequency of 200 kHz and a pulse fraction of 20%. Ex. 1 and Ex. 2 are the experimental results obtained from different needle tip specimens. The measurement in laser-mode was conducted with a pulse frequency of 250 kHz.

In voltage-mode (Fig. 1(a)), the apparent concentration of solute copper changed significantly with the specimen temperature, and the concentrations obtained at 40 K and below exceeded the actual concentration. The apparent concentration significantly decreased with increasing specimen temperature. In contrast, in laser-mode, the change in apparent concentration with temperature was much smaller than that in voltage-mode. The concentration never exceeded the actual concentration, even at low temperature of 20 K, and it hardly decreased at higher temperatures. Quantitative analysis performance was nearly obtained at higher values of laser pulse energy, even at high temperatures. The pulsed laser atom probe showed rather better quantitative performance over a wide range of temperatures than the pulsed voltage atom probe.

Fig. 2 shows the temperature dependence of the single charged Cu⁺ ion ratio in voltage-mode and laser-mode, where the Cu⁺ ion ratio was defined as Cu⁺/(Cu⁺+Cu²⁺). The Cu⁺ ratio is known to increase as the evaporation field lowers according to the post ionization model [26–28]. The charge state of field evaporated ions is also influenced by other measurement conditions, and thus, the laser-mode and voltage-mode evaporation processes cannot be directly compared one-to-one. However, a relative comparison of each mode is possible. The difference in the Cu⁺ ratio between Ex. 1 and Ex. 2 is probably due to the difference in crystallographic orientation. The Cu⁺ ratio actually increased with the specimen temperature in voltage-mode from 0.05 at 20 K to 0.58 at 80 K. On the other hand, the data obtained in laser-mode showed a rather high Cu⁺ ion ratio, which supports the view that field evaporation in laser-mode is generated due to an instantaneous rise in the tip surface temperature caused by the pulsed laser radiation. The Cu⁺ ion ratio increased with increasing laser pulse energy, but there was little dependence on the specimen temperature. This result implies that the surface temperature of the tip apex during field evaporation in laser-mode was sufficiently higher than the specimen base temperature [29,30].

Fig. 3(a) shows a comparison of the mass spectra between the voltage-mode and laser-mode at 60 K, and Fig. 3(b) shows a comparison of the mass spectra obtained in laser-mode at a laser pulse energy of 0.6 nJ at various specimen temperatures. The peaks in voltage-mode have a more symmetric shape, while the peaks in laser-mode have a large tail in the direction of higher mass. With increasing pulse energy and decreasing specimen temperature, the tails of the Fe²⁺ peaks decreased, and the background noise also dropped [31]. It is difficult to quantitatively separate the peaks of Fe²⁺ isotopic ions due to the presence of the tail in laser-mode.

4. Discussion

4.1. Voltage-mode

First, we will discuss the cause of the deviation from the actual concentration in voltage-mode (Fig. 2a). As mentioned above,

Download English Version:

<https://daneshyari.com/en/article/5466827>

Download Persian Version:

<https://daneshyari.com/article/5466827>

[Daneshyari.com](https://daneshyari.com)