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The study of quantitativeness in atom probe analysis of alloying elements in steel

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ABSTRACT

The quantitativeness in atom probe analysis of dilute solute alloying elements in steel was systematically investigated. The samples of binary Fe–Si, Fe–Ti, Fe–Cr, Fe–Cu, Fe–Mn and Fe–Mo alloys were prepared for present study. The apparent compositions of alloying elements were examined by three-dimensional atom probe (3DAP) under various experimental conditions. The temperature dependence of the apparent compositions varied largely with the alloys, which indicated that the degree of preferential evaporation or retention varied with the alloying elements. Furthermore, the analysis direction dependence of the apparent Mn composition was examined in the Fe–Mn alloy. The experimental results indicated that the order of the field evaporation rate of elements in steel was Cu > Cr > Mn~Mo > Fe > Ti~Si. The field evaporability of alloying elements in steel was discussed in terms of the solution enthalpy of the alloying elements and the phase types of the binary Fe alloys.

1. Introduction

Three-dimensional atom probe (3DAP) has great advantages in the nano-scale characterization of materials such as segregation, partitioning, precipitation and solid solution. These features directly affect the microstructures and the mechanical properties of materials [1,2]. The 3DAP is used to characterize the small features in steel materials. However, some anomalous behavior has been reported in the quantitativeness in the atom probe analysis for decades. Miller and Smith [3] showed that the Si composition deviated from accurate composition to higher composition in Fe–3 wt%Si alloy at lower pulse fraction, higher specimen temperature and lower pulse repetition rate. It was further explained that the deviation was caused by the preferential removal of Fe atoms during the "Pulse off" part of the operating cycle. Opposite to Si, Worrall and Smith [4] showed that the apparent composition of Cu in Fe–0.6 wt%Cu alloy deviated lower than the accurate composition of that depending on the experimental conditions. These two reports also indicated that the analysis direction affected the quantitativeness of the alloying elements. Recently, Miller and Russell [5] reported that the preferential evaporation was substantially reduced due to the smaller proportion of time spent at the standing voltage using a local electrode atom probe with a high pulse frequency.

It is important to understand these deviation trends for alloying elements in steel for the characterization of steels using 3DAP. This study aimed to systematically understand the trends and the origin of quantitativeness in 3DAP analysis of all the important alloying elements in steel.

2. Experimental

2.1. Samples

Solution-treated binary Fe–6.26 at%Si, Fe–1.88 at%Ti, Fe–1.08 at%Cr, Fe–1.23 at%Cu, Fe–0.51 at%Mn and Fe–0.26 at%Mo model alloys specimens were prepared to examine the apparent composition by the atom probe. All the alloys had ferrite single phase and the alloying elements were distributed homogeneously in solid solution. These alloys were mechanically cut into 0.3 mm × 0.3 mm × 10 mm rods and then electropolished to the needle specimens.

2.2. Experimental conditions

An energy-compensated 3DAP with a delay line detector (Oxford nano Science Ltd.) was used for these experiments. The

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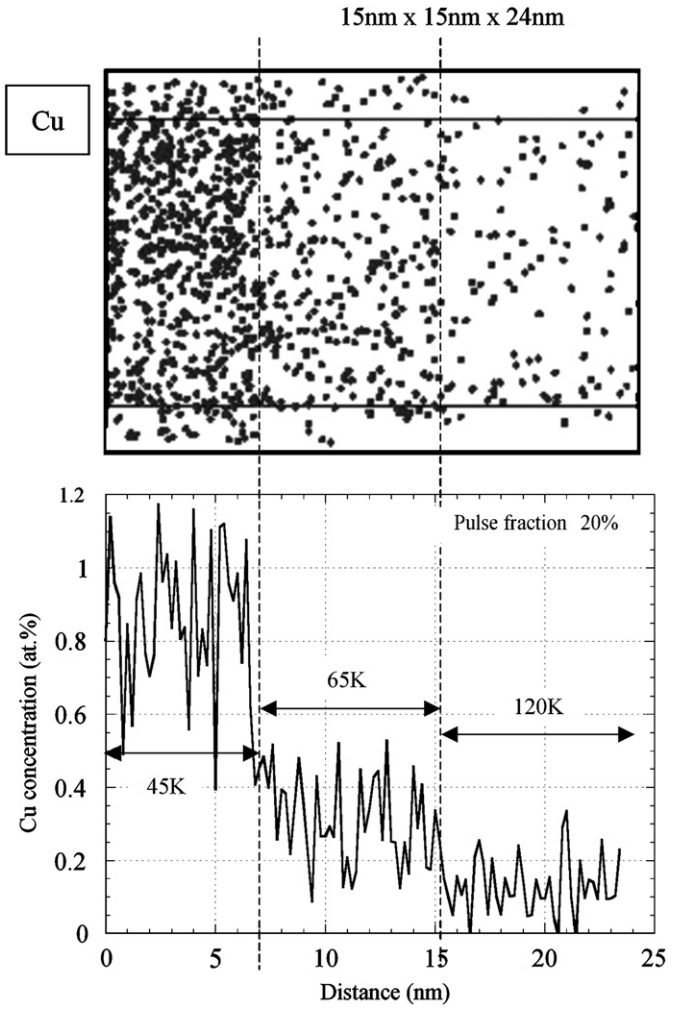

Fig. 1. A 3D elemental map and a concentration profile of Cu in Fe–1.23at%Cu at a specimen temperatures 45, 65 and 120 K.

analysis was performed under various conditions. The pulse fractions and the specimen temperatures were varied from 5% to 30% and from 45 to 120 K, respectively. Fig. 1 shows an example of a 3D elemental map and a concentration profile of Cu at the specimen temperatures of 45, 65 and 120 K in the Fe–Cu alloy. In order to examine the temperature dependence accurately, the continuous analysis of the same specimen tip was conducted under the same condition of pulse fraction and analysis direction while the specimen temperature was changed. The pulse frequency was set to be 1.5 kHz. The analysis direction was basically oriented near the (1 1 0) pole. In each condition, 100,000 ions or above were collected to obtain compositions with a little standard error less than that of 0.08 at% [6]. Furthermore, a large angle atom probe with a pulse frequency of 2 kHz was used to investigate the influence of analysis direction.

The Fe–Si alloy was used to examine the pulse fraction and all the alloys were used to examine the specimen temperature dependence of the apparent composition.

3. Results and discussion

3.1. Pulse fraction dependence in Fe–Si alloy

Fig. 2 shows the pulse fraction dependence of the apparent Si compositions in the Fe–Si alloy at 65 K. The broken line indicates

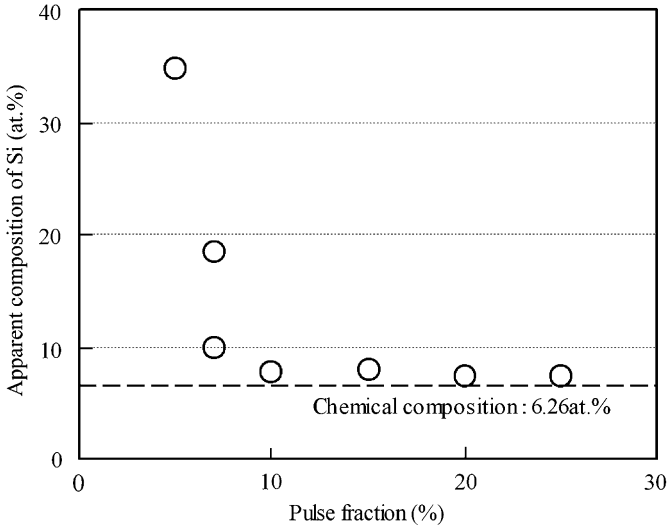

Fig. 2. Pulse fraction dependence of apparent Si composition at 65 K.

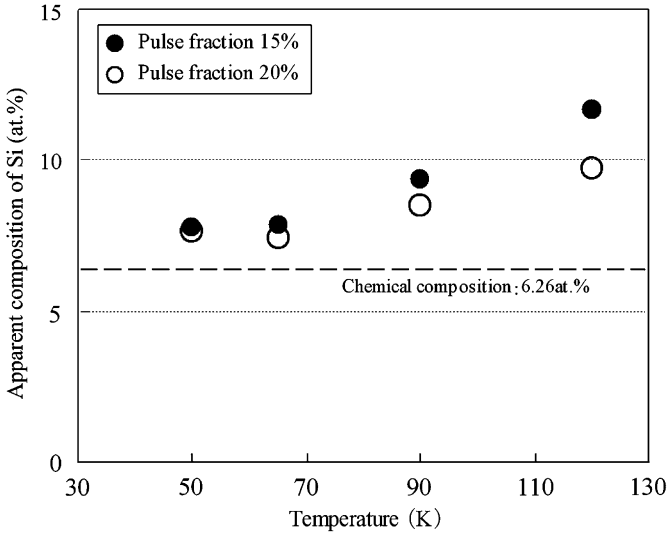

Fig. 3. Specimen temperature dependence of apparent Si composition.

the chemical composition of the alloy. Low pulse fractions caused the apparent Si composition to deviate to higher composition. Under pulse fractions of 10% or less, normal operation could not be conducted and the apparent compositions deviated abnormally. The result agrees with the earlier researches [3]. Therefore, high-pulse fractions over 15% were applied to examine the specimen temperature dependence of the quantitativeness in all the model alloys.

3.2. Specimen temperature dependence in the model alloys

Fig. 3 shows the temperature dependence of the apparent Si composition at pulse fractions 15–20%. The apparent compositions obtained upon analysis were in better accord with the chemical composition at low temperatures. The apparent composition increased largely with increase in the temperature. The apparent Cu compositions were also in better accord with the chemical composition in the Fe–Cu alloy at low temperatures as shown in Fig. 1. However, the apparent Cu composition drastically decreased with increase in the temperature contrary to Si.