Evaluation of TES microcalorimeter EDS for low-concentration phosphorus detection in steels

Yamada, K.[1], Kawakami, N.[1], Ichihara, C.[1], Okazaki, Y.[2], Ii, S.[3], Ohmura, T.[3] and Hara, T.[3]

[1] Applied Physics Research Laboratory, Kobe Steel, Ltd., Japan, [2] Materials Research Laboratory, Kobe Steel, Ltd., Japan, [3] Research Center for Structural Materials, National Institute for Materials Science, Japan

Detection of alloying elements in steels with high precision is becoming increasingly important in materials design to control its physical properties. Phosphorus is one of the critical elements which drastically affects mechanical properties. It is well known that phosphorus segregates at grain boundaries during heat treatment and the enrichment of phosphorus reduces the cohesive strength between grains, resulting in brittle failure.

Transmission electron microscope (TEM) with energy-dispersive X-ray spectrometer (EDS) is widely used for quantitative analysis of elements in materials, i.e., at a specified point such as grain boundaries or fine precipitates in steels. However, the energy resolution of a silicon drift detector (SDD) is typically around 125 eV, which is still insufficient to analyze such small amount of elements. Recently, a STEM-EDS system with an X-ray detector applying a superconducting transition-edge sensor (TES) microcalorimeter has developed. Since, this detector shows high energy resolution, below 10 eV, higher sensitivity of a detection limit is expected.

In this paper, STEM-EDS combined with the TES microcalorimeter was applied for detection of phosphorus in steels, and the detection performance was also evaluated. An Fe-P-Mo-Mn alloy was used for evaluation, which was heat treated at 1273 K for 1 hour followed by quenching in water. Then, it was divided into two samples according to the following thermal treatment: a) as water quenched (WQ) and b) step cooling heat treatment (SC) with a typical operation used by the American Petroleum Institute (API). The both samples were processed as thin film specimens with thickness about 100 nm by FIB. Measurements were done by the TES microcalorimeter EDS system and by a double-SDD (JEOL JEM-2800) system for comparison.

In the SC sample, the phosphorus detection at the grain boundaries was compared between the TES microcalorimeter and the double-SDD. In the TES spectrum, phosphorus Kα was precisely detected as a separated peak at 2013 eV, whereas only a broad band was observed in the SDD spectrum. The results show the high energy resolution of the TES (ΔE<10 eV) has a potential for precise analyses of trace amounts of elements in steels. In order to evaluate the detection limit of the TES microcalorimeter, measurement was done over a long period of time for the WQ sample, where lots of X-ray counts were accumulated. Comparing the TES spectra for every several hours, the variation of background counts obviously decreases with time, resulting in improvement of detectability. The detection limit was estimated by the minimum mass fraction (MMF). Assuming the phosphorus concentration in the WQ sample is 0.012 wt%, which was determined by a fluorescent X-ray analysis, the MMF of phosphorus is calculated to be down to 0.005 wt%. The results successfully explain that higher energy resolution of EDS is effective for lowering the detection limit. It is expected that the TES microcalorimeter is able to expand its application in variety of elements, not only phosphorus, and contributes to accelerate material developments.