Direct metallographic analysis of an iron meteorite using hard x-ray photoelectron emission microscopy

The local structure of an iron meteorite was analyzed using photoemission electron microscopy (PEEM) and hard x-rays. The x-ray absorption fine-structure spectrum was obtained for each pixel in the PEEM image. The spectrum provides a wide variety of information, e.g., chemical composition, electronic structure, and lattice structure, in the interface region of the Widmanstätten structure. The shape of the absorption edge and the radial distribution function indicate that the structural phase changes from body- to face-centered cubic phases as the Ni composition at the interface is increased. The use of PEEM and hard x-rays is an attractive approach for local structure analysis.

Introduction

The iron meteorite described in this paper shows a unique extraterrestrial pattern, which is referred to as the Widmanstätten structure. Its metallographic fine structure is characterized as a mixed crystal composed of body-centered-cubic (bcc) and face-centered-cubic (fcc) FeNi phases from the viewpoint of material science [1–4]. Planetary scientists believe that the meteorite under discussion was formed in an asteroid’s core, meaning that it was heated during the formation of the solar system and then cooled extremely slowly because of the thermal insulation effect of the silicate mantles. The diffusion coefficients of Fe and Ni under these unique thermal conditions for more than 4.6 billion years produce the Widmanstätten structure, which consists of elongated Fe-Ni microcrystals with fine interleaving of the α and γ FeNi bands, or ribbons, called lamellae.

The metallographic characterization of the Widmanstätten structure has been conducted using various evaluation techniques, including x-ray diffraction (XRD) and scanning electron microscopy (SEM). Macroscopic XRD, for example, yields accurate lattice constants without spatial information [4]. SEM provides real-space images without lattice information. In this study, we used photoemission electron microscopy (PEEM) with hard x-rays to directly and simultaneously visualize the shape, chemical composition, electronic structure, and lattice structure of a Gibeon iron meteorite.

PEEM is a powerful imaging technique with a resolving power value of several tens of nanometers, which is capable of resolving the spatial distribution of photoemitted secondary electrons [5, 6]. The intensity of the photoelectrons is proportional to the x-ray absorption intensity, and continuous scanning of photon energy extracts the x-ray absorption fine-structure (XAFS) spectrum for each pixel in the observed image. The XAFS spectrum provides a wide variety of information such as chemical composition, electronic structure, and lattice structure. Therefore, hard x-ray PEEM (HX-PEEM) allows for the possibility of a high-resolution full-field direct characterization of the local structure of solids [7]. The magnetism of the meteorite was previously investigated by PEEM [1, 8–12]. In this paper, we report the first application of HX-PEEM to the analysis of the metallographic properties of the Widmanstätten structure in an iron meteorite.

Experimental

The Gibeon iron meteorite is a typical iron meteorite exhibiting the Widmanstätten structure. The surface was carefully prepared using an automatic mechanical polisher.
(Musashino Denshi MA-150 with an MS-2), a 6-µm diamond slurry for rough polishing, and a 1-µm diamond slurry for mirror-finish polishing. The specimen was sliced nearly parallel to the (001) \textit{bcc} plane of the \textit{C11} lamella.

The PEEM measurement system was connected to the third-generation hard x-ray undulator beamline (BL39XU) at SPring-8 [13, 14]. The experimental setup is described in detail elsewhere [7]. Briefly, the PEEM chamber was placed in the experimental hatch, and the position of the PEEM analyzer was remote controlled from outside the hatch to align the beam position to the PEEM viewing field. The position of the hard x-ray was accurately stabilized using a monochromator stabilization module [15]. The photon flux of BL39XU reaches $2 \times 10^{13}$ photons/s, and the typical beam size is 0.6 × 0.6 mm. A four-quadrant slit was used to trim the beam to fit the PEEM viewing field. This was done

Figure 1

SEM and PEEM images. (a) SEM image observed for the $\alpha$ and $\gamma$ lamellae in the Widmanstätten structure of the Gibeon iron meteorite. (b) PEEM image observed for the interface region marked by circle in Figure 1(a). (c–i) Mask patterns for extracting the XAFS spectrum for various Ni compositions: (c) the whole $\alpha$ lamella, (d) 32.5% in the $\gamma$ lamella, (e) 30%, (f) 27.5%, (g) 25%, (h) 22.25%, and (i) 20%.
because preventing entry of stray electrons from outside the viewing field improves the signal-to-noise ratio of the XAFS spectrum. The nominal spatial resolution of the PEEM apparatus is 35 nm. For a viewing field of 50 μm, one pixel corresponds to 100 nm. The typical exposure time per image was 10 seconds, and 421 images were obtained in the energy range from 6.90 to 7.80 keV for Fe and from 8.12 to 9.02 keV for Ni. The cross section of the K shell of a 3d metal usually becomes smaller in the hard x-ray region, but the high power of the third-generation undulator and the accurate beam stabilization enabled us to obtain a sufficient photoelectron yield. The Ni composition was qualitatively estimated on the basis of the edge jump of the XAFS spectrum at the K edge and quantitatively calibrated using the data obtained by electron-probe microanalysis.

**Results and discussion**

Figure 1(a) shows an SEM image of the Widmanstätten structure; α lamellae are separated by a 40-μm-wide γ lamella. The Ni spatial distribution for the boundary region marked by the circle was obtained by HX-PEEM. As shown in Figure 1(b), the Ni composition for the α lamellae was fairly constant at 6.6%, whereas that for the γ lamella steadily increased from 10% to 35% toward the interface. This is the typical distribution of Ni in an iron meteorite. Note that Ni was densely concentrated at the boundary of the laminated Fe-Ni thin films.

To examine the local metallographic structure, we extracted the spatially resolved XAFS spectrum from the viewing field using mask patterns, which were defined as selected pixels in the observed image. We used the whole region of the α lamella, as shown in Figure 1(c), and varied the Ni composition for the γ lamella from 32.5% to 20%, as shown in Figure 1(d)–(i). Absorption intensity was taken as the intensity averaged over the pixels in the region of interest, and the intensity was recorded as a function of the photon energy of the irradiated x-rays in order to obtain a spectrum.

The spatially resolved XAFS spectrum obtained for the interface region in Figure 1(b) is shown in Figure 2(a). The XAFS raw spectrum was extracted from the specified pixels as a function of the Ni composition (20%, 22.5%, 25%, 27.5%, 30%, 32.5% ±1.25%). As shown in the inset in Figure 2(a), the spectral profile at the Fe K edge changed from a single to a suppressed peak on the crest as the Ni content increases. This indicates that the crystal structure changed because of the structural transition from bcc to fcc, which is commonly observed when the Ni content is near 25% [16]. This suggests that the spectral change at the absorption edge represents a structural phase transition near the interface.

To clarify the local structure in the boundary region, we carried out an extended XAFS analysis for various Ni compositions in the γ lamella and applied the Fourier transform to the XAFS spectrum. This transform represents the radial distribution function (RDF) around the absorbing
atom. As shown in Figure 2(b), the RDF varied with the Ni composition. The distances of the second and third neighbors in the RDF were used to distinguish between the bcc and fcc structures. The RDF profile systematically varied with the Ni composition. The two peaks at approximately 3.3 and 4.4 Å for the 20% Ni-Fe agree well with those for the bcc Fe foil used as reference; the third neighbor peak gradually shifted to a shorter distance as the Ni composition was increased. The RDF of the 35% Ni-Fe is consistent with that of the fcc Fe-Ni alloy [17, 18]. This finding that the structural transition bcc-fcc occurs with a variation in the Ni composition means that Ni diffusion toward the interface accounts for the spatial distribution in the crystallographic structure.

Conclusion
Using a combination of PEEM and hard x-rays, we have analyzed the local structure of an iron meteorite. Spatially resolved XAFS spectra were obtained for the Fe K-absorption edge by continuous photon energy scanning and analytical extraction of the absorption intensity. Both the shape of the absorption edge and the RDF indicate that the structural phase changes from bcc to fcc as the Ni composition at the interface is increased. Application of PEEM with hard x-rays is thus a promising approach to local structure analysis.

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