On the structure of cleaved surfaces in biotite mica

Toshihiro KOGURE

Mineralogical Institute, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract

Cleaved surfaces in biotite mica have been investigated using high-resolution TEM with the beam direction parallel to the cleaved surfaces to reveal the location of some potassium ions. Numerous (001) cleavages were formed along thin edges of the crystals, probably due to tensile strain induced by ion milling sample preparation. The cleavages are formed at interlayer positions in the biotite structure and opposing cleavage surfaces have distinct contrasts in atomic-resolution electron micrograph. In part, the contrast difference is explained by multislice image simulation calculated for the model where a certain amount (about half a monolayer in the maximum) of potassium ions are located on one side of the cleavage and few potassium ions are located on the other side. Some cleavages are healed by beam radiation, leaving no trace in the structure image of the recovered interlayer, indicating diffusion of potassium into the interlayer from the specimen surfaces.

Introduction

Although crystal structures of most minerals have been determined precisely using X-ray structure analyses, surface atomic structures of minerals are poorly understood. To investigate the surface of minerals or crystals, low-energy electron diffraction (LEED) has been used historically and scanning probe microscopy (SPM) is commonly utilized recently (Hochella, 1990).

Cleaved mica surfaces have been extensively used as a substrate material, especially for early epitaxial vapor deposition studies. Among these studies, several groups had an interest in the surface structure and composition of mica itself for further investigations of epitaxial phenomena (Müller and Chang, 1968, 1969; Poppa and Elliot, 1971; Caslavsky and Vedam, 1971). As well known, the mica structure consists of two tetrahedral sheets and one octahedral sheet between them as a unit, which is often designated as TOT (tetrahedral-octahedral-tetrahedral) layer or talc-like layer, and a space between two TOT layers (called an interlayer), where alkali or alkaline-earth cations exist as interlayer charge. The (001) cleavage is perfect and it is formed at these interlayer positions. Müller and Chang (1968, 1969) first discussed the location of these interlayer cations when a mica crystal is cleaved. Using

low-energy electron diffraction (LEED) and other techniques, they concluded that half a monolayer of potassium ions resides on the both of cleaved surfaces and they are arranged randomly on half of the centers of pseudo-hexagonal oxygen ring. Several papers accepted this conclusion for subsequent experiments without discussion (Caslavsky and Vedam, 1971; Reichelt, 1975).

Besides the surface analyzing techniques mentioned above, the surface structures or compositions of crystals have been investigated using high-resolution TEM. Commonly, observations with the electron beam parallel to the surface have been reported for various compounds (e.g., Marks, 1984; Marks and Smith, 1984; Iijima, 1984; Tanji and Cowley, 1985). However, no study of surfaces of mica or other related sheet silicates has been reported with a sufficient resolution to reveal atomic structures of surfaces. Besides the utilization as substrates for thin film deposition, surfaces of mica or related sheet silicates are important for earth science because of their abundance in sediments or soils. This paper reports HRTEM images of cleaved surfaces in mica and discusses their atomic structure.

Sample and Methods

The investigated sample is biotite, ferromagnesian trioctahedral mica, from Nellor pegmatite mine, India. The reported chemical composition of the sample by wet analysis is $(K_{0.83}Na_{0.05})(Mg_{0.50}Fe^{2+}_{1.58}Fe^{3+}_{0.05}Al_{0.57}Ti_{0.11})(Si_{2.68}Al_{1.32})O_{10}(OH)_2$ (reported by Nichika Corporation, Japan). The reason to use this sample is that biotite is more resistant to beam radiation than other mica, e.g., muscovite (Iijima and Zhu, 1982), phlogopite, phengite, etc. (Nespolo and Kogure, 1997). Preliminary HRTEM observations indicated that the sample contained no potassium depleted interlayers, which are often observed in weathered or altered mica (Kogure and Murakami, 1996). As mica possesses platy character due to the perfect (001) cleavages, oriented thin specimens should be prepared and viewed with the electron beam parallel to the (001) surface in a TEM. Several cleaved mica fragments were attached together with epoxy resin. Then they were sliced and thinned using ion-milling as is used for conventional cross-sectional TEM observation. However, the contrast of these cleaved surfaces, or the boundary between the crystal and epoxy resin, was not clear enough to distinguish surface alkali cations. On the other hand, many fine cleavages were formed along thin edges of the specimen, as described below. These fine cleavages were suitable to investigate the surface structure because both sides of a cleavage can be recorded in a image with the same crystal thickness and defocus values, which enables simultaneous comparison of both sides of the observed surface images with simulated images. The sample was coated with a carbon thin film (~20 nm thick) to prevent specimen charging in the TEM.

TEM observations were performed using JEOL JEM-2010 microscope with nominal Cs value of 0.5 mm and operated at 200 kV. Several images were processed to remove the contrast from amorphous materials using rotational filtering (NCEM package of Kilaas and Siddnei implemented within DigitalMicrograph version 2.5, Gatan Ltd.). Multislice image

FIG. 1. (a) A low magnification image around an edge of the biotite crystal. Nearly periodical fine cleavages are observed. Note amorphous material along the edge is not split at the cleavage position. (b) diffraction patterns taken from an area between two cleavages near the edge (upper) and inside the crystal where no cleavage is formed (lower). The incident beam used was 100 nm in diameter. The upper pattern has a slightly larger interval, namely a smaller layer unit length by about 2%.

simulations were performed using the MacTempas software (Total Resolution Co.).

Results and Discussion

The diffraction patterns and HRTEM images indicate that this biotite adopts basically $2M_1$ polytype structure. However, stacking disorder with local 3T sequence is common. Fig. 1a shows a low magnification image around an edge of the specimen. Near the edge, many fine slits, which are (001) cleavages, are observed. Diffraction patterns using a small (~ 100 nm) incident beam from a cleaved region near the edge indicate a slight decrease (about 2 %) of the unit length along c^* axis compared to neighboring inner, non-cleaved region (Fig. 1b). This result suggests that these fine cleavages were formed by shrinkage of the biotite crystal near the edge. It is supposed that the argon sputtering during ion-milling sample preparation forms many lattice defects (vacancy sites) near the surfaces of the crystal to generate tensile strain. The cleavages at thin areas were formed to release such tensile strain. However, such numerous cleavages have not been observed in our other specimens of micas or other layer silicates investigated so far using the same sample preparation methods. Some unidentified intrinsic characteristics of this sample may also contribute to the formation of the cleavages. On the other hand, the amorphous material, which is observed closest to the edge, is not split at the cleaved points as shown in Fig. 1a. As well known, this amorphous material was formed at the surfaces of the specimen by ion-milling. If the cleavages were formed

during ion-milling, this amorphous material must be also split. This suggests that cleavages were generated at the thin crystal region to release tensile strain (such strain does not exist in amorphous material) after the ion-milling was finished. This is probably analogous to the phenomenon that strained thin films are often peeled from substrates gradually in atmosphere after the deposition in vacuum. No apparent relation between the stacking sequences of biotite crystals and locations of cleavages was observed by the investigation of several HRTEM images.

Fig. 2 shows the crystal structure model of biotite ($2M_1$ polytype) along $[110]$ direction, corresponding calculated HRTEM image (parameters used are described in the figure caption), and a typical experimental image. Locations of each cation sheet (Si/Al tetrahedral sheet, Mg/Fe octahedral sheet and potassium at the interlayer) are clearly recognizable in both images. The positions of the black dots in a tetrahedral sheet, which correspond to SiO_4 zigzag chains along the observation direction reflect the stacking sequences. All high-resolution photographs (e.g. Fig. 2) were taken after this characteristic image contrast was visible on the CCD camera system.

Fig. 3a shows a HRTEM image around a cleavage and the corresponding rotationally filtered image (Fig. 3b). The amorphous material inside the cleavage in Fig. 3a is regarded as the carbon film coated on the specimen. It is obvious that the contrast of two sides are different from each other.

This is especially apparent after removal of the contrast from amorphous material by the filtering although there is a faint, artifact contrast caused by the filtering at the center space (Fig. 3b). About fifteen HR images around cleavages in a crystal were investigated and they were similar to images in Figure 3 although some of them showed less distinct difference of

FIG. 2. Comparison of (a) the structure model of biotite ($2M_1$) observed from the $[110]$ direction, (b) the corresponding calculated image using the MacTempas program and (c) an observed image. The thickness of the crystal and defocus value used for the calculation are 5 nm and -32 nm (underfocus) respectively.

FIG. 3. (a) HRTEM image around a cleavage and (b) its processed image around the center part of (a) using rotational filter.

the contrast between two surfaces than that in Fig. 3. To test the inference that contrast at the surfaces in Fig. 3 is due to uneven distribution of potassium on the two surfaces, multislice image simulations were performed. Fig. 4 indicates a simulated image of the interlayer surfaces with various values for the occupancy of potassium located on one surface. Changing the number of potassium along the beam direction revealed the same effect to the image contrast as varying the occupancy parameter of potassium site. The crystal thickness and defocus value were selected to match the contrast inside the crystal to that in the observed image in Fig. 3. Although several other parameters (small displacements of surface potassium position, Debye-Waller factor for potassium, etc.) for the image simulation were changed, the calculated images were almost identical with reasonable parameter ranges. Large tilts of the crystal changed the calculated images of the surface. However, such tilts could not reproduce the observed contrast inside the crystal simultaneously. If no potassium resides at a surface (the occupancy is zero), the surface is terminated with black dots corresponding to the tetrahedral sheet at the surface and these dots become slightly larger than those inside the crystal due to surface effect. This is observed at the surface in the left of the observed image in Fig. 3, indicating there are few potassium ions on this side. As the occupancy of surface potassium is increased, black dots due to potassium appear, with distinctive white spots between them. When the occupancy exceeds about 0.75, the black dots associated with surface potassium are stronger than those corresponding with K inside the crystal (see Fig. 4). At the surface contrast in the right side of the observed image in Fig. 3, white spots are clearly observed and black dots corresponding to potassium ions are weaker than those inside the crystal. Comparing the observed and the calculated images, it is roughly estimated that the occupancy of potassium at the observed surface is close to but

FIG. 4. Calculated images for the biotite surface with various surface potassium occupancies. The defocus value is -32 nm and the crystal thickness is 5 nm. These values are selected to reproduce the observed contrast inside the crystal.

FIG. 5. (a-d) HRTEM images of several cleavages and (e) the low magnification image to show the locations of these cleavages. Note that the white surface contrast are formed on the same side in these cleavages as indicated by the arrow heads.

does not exceed 0.5. This result is concordant with that suggested in the previous works (Müller and Chang, 1968, 1969) as mentioned above. However, in this study few potassium ions are located on the other side of the cleavages. This result indicates that the cleavages occurred unsymmetrically with respect to potassium ions. It is supposed that in the initial state of cleavage most potassium ions attach only on one side and then a part of them diffused away from the cleavage surface to realize charge neutralization. As mentioned above, the cleavages are considered to have formed in the atmosphere after ion-milling. Probably other charged ions (proton, etc.) adsorbed on the side where few potassium ions reside. The reason for this uneven distribution of potassium ions is not clear. It is unlikely to occur if we consider the symmetry of the potassium site in the biotite structure. However, local structures in the crystal may not be the same as the averaged one determined by X-ray structure analyses. For instance, the charge of tetrahedral sheets can be fluctuated in the crystal to attract

or repel potassium ions.

The surface which has the similar contrast is in the same side among neighboring cleavages, as shown in Fig. 5. In this figure, all cleavages have the bright surface contrast in the right side. Furthermore, in all cleavages investigated in the crystal, that are about fifteen as mentioned above, the surface which has the white contrast is the right side in all cases.

It was observed that sometimes strong beam irradiation induced healing of small cleavages at the edges of the crystal, accompanied by expansion of the neighboring cleavages. Fig. 6 is a low magnification image showing this phenomenon. The small cleavage indicated by the arrow has been healed, whereas the other two cleavages have been expanded (Fig. 6). The strength of beam was the order of 1 A/cm^2 on the sample and radiation time was several seconds between Fig. 6a and 6b. The HRTEM images are shown in Fig. 7. In Figs. 7a and 7b, the two sides at the cleavage have the similar contrast to those in Fig. 3.

As shown in Fig. 7c, the contrast of the healed interlayer is almost the same as those of other interlayers. Kogure and Murakami (1996) reported that the difference of site occupancy of potassium ion is distinguishable to some extent by the contrast at the interlayer in biotite. Despite the estimated half a monolayer of potassium associated with cleavages, the above result indicates that the occupancy of potassium ions recovered to close to 1.0 when the cleavage was healed. It may be that other potassium ions are supplied from outside the cleavage surface, for instance, specimen surface, etc. by diffusion. Amorphous carbon film on the cleaved surface may also have diffused away when the cleavage was closed.

FIG. 6. Low magnification images around an edge (a) before and (b) after strong beam radiation. The small cleavage indicated by the arrow is healed whereas the large one in the left side is expanded.

FIG. 7. HRTEM images to show the healing of a cleavage by strong beam radiation. Rotational filter was applied to all images. The contrast of the recovered interlayer in (c) is perfectly identical to those at adjacent interlayers.

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