

TEM Observation of Interstratified Ni-Serpentine/Smectite Compounds

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Interstratified Ni-serpentine/smectite = 2/1 compound was described by transmission electron microscopy (TEM) for the first time. The image of the lattice fringe coincided with the result of simulation, and it is clearly different from that of chlorite/smectite = 1/1 mineral which has a similar periodicity in X-ray diffraction pattern. The image of domains curving to the direction of their serpentine-part, suggested that the surface of the particle was mainly consisting of Si-O sheets.

Ni-Serpentine ($(\text{Ni}_{3-a}\text{Al}_a)(\text{Al}_a\text{Si}_{2-a})\text{O}_5(\text{OH})_4$) and Ni-smectite ($(\text{Na}_b\text{Ni}_3(\text{Al}_b\text{Si}_{4-b})\text{O}_{10}(\text{OH})_2$) are both in the family of phyllosilicate minerals. Smectite can be described simply on the basis of two Si-O tetrahedral sheets sandwiching a sheet of octahedral Metal-OH. On the other hand, serpentine has one Si-O and one Metal-OH sheet. Smectite swells in the water due to its layer charge, while serpentine does not.¹ Interstratified phyllosilicates can be found in natural deposits and sediments in many forms, i.e. kaolinite/mica, chlorite/smectite, chlorite/serpentine, etc., although, there have been no reports about natural interstratified serpentine/smectite interstratified minerals.² For the first time, Torii et al. described the hydrothermal synthesis of interstratified serpentine/smectite = 3/1 – 1/3 compounds from Si-Al-(Mg, M) hydrous oxide (M = Ni, Co, Cu and Zn). According to them, the rate of the decrease of the methylene blue (MB) adsorption with increase in the serpentine/smectite ratio was much less than those estimated from the ideal structure. Those interstratified serpentine/smectite compounds also showed the extra viscosity in sea water and in acid water and can act as mesoporous catalysis after drying at 300 °C.^{2,3} However, only X-ray diffractometry was used for the determination of their structures except for 1/1,^{2,3} and the relationships between those behaviors and their structures still have not been clear. In this study, interstratified Ni-serpentine/smectite compounds were identified by TEM and their surface structure was discussed on the image of the lattice fringe comparing with the calculated image.

The Si-Al-Ni hydrous oxides of atomic ratio Si-Al-Ni = 7.22-0.78-7.54 for sample 1 and Si-Al-Ni = 5.7-0.3-6.0 for sample 2 were prepared as starting materials of the syntheses. The hydrous oxide was dispersed in water and hydrothermally treated at 250 °C for 24 h. Products were examined by X-ray diffractometry (XRD), Transmission electron microscopy (TEM). Computer simulation was also carried out by MachREM (AI-SPEC co. Ltd.) using condition at Cs = 1.9 mm and number of the slice = 16.

To get the image of layering, the samples of serpentine/smectite mixed compounds were layered on an OHP film and dried at 100 °C for 1 day. After drying, the sample on the film was cut about 2 mm width and raised with resin in beam capsule. Then after polymerizing the resin with evacuat-

ing at 80 °C, the sample with film and resin was cut using Ultra Microtome. TEM observation was carried out using JEOL JEM2000EXII at an accelerated voltage of 200 kV.

The X-ray oriented diffraction patterns of the synthesized samples are shown in Figure 1. Sample 1 was found to be interstratified serpentine/smectite = 1/1 compound with the d(001) spacings of 22.4 Å. After the treatment with ethylene glycol the d(001) spacings expanded to 24.4 Å, which distinguishes sample 1 from interstratified chlorite/serpentine = 1/1 mineral. On the other hand, d(001) spacing of the sample 2 was 27.5 Å, and expanded to 32.6 Å with ethylene glycol, which does not differentiate interstratified serpentine/smectite = 2/1 compound and interstratified chlorite/smectite = 1/1 mineral.

TEM showed that sample 1 and sample 2 had almost similar particle sizes of 300-500 Å in ab-plane. Figures 2 and 3 are the lattice image parallel to c-axis of sample 1 and sample 2. Figure 2 shows 1-4 cycled interferential fringe with 17.5 Å periodicity (smaller than that from XRD due to dehydration), coincided with the calculated images based on the structure consisting of serpentine-part (A) and smectite (mica) -part (B)

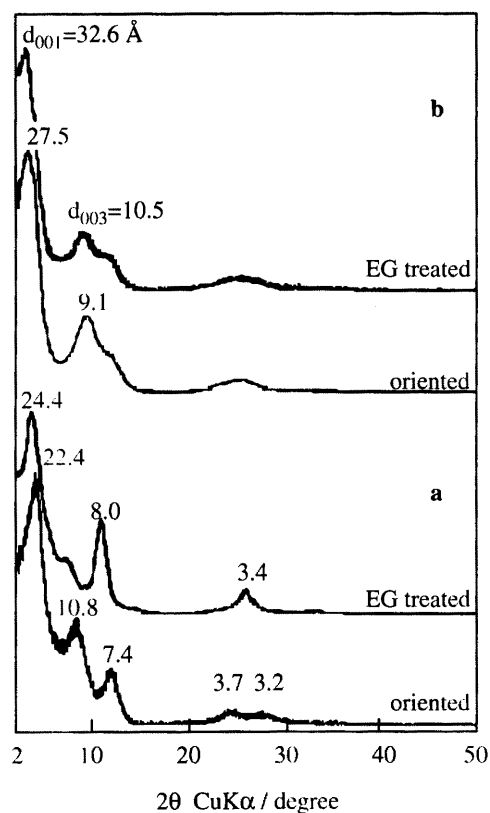


Figure 1. X-Ray diffraction patterns of sample 1 (a) and sample 2 (b) each oriented and treated with ethylene glycol (EG) solution.

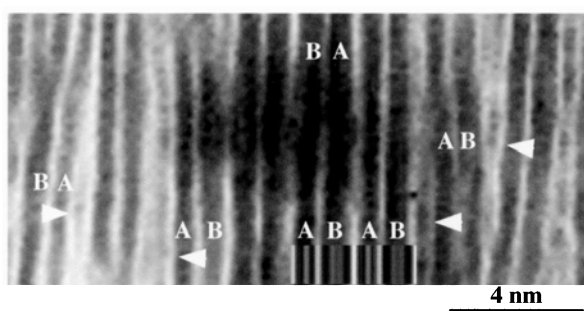


Figure 2. The lattice fringe of the sample 1 obtained by TEM and the image of interstratified serpentine/smectite = 1/1 compound simulated by MacHREM under the condition of defocus = 870 Å. One domain has two black fringes of 7 Å and 10 Å, each corresponds to the serpentine-part (A) and the smectite-part (B). The parts A and B in a domain seem to rotate partially. Some domains are curving in the direction of the arrows.

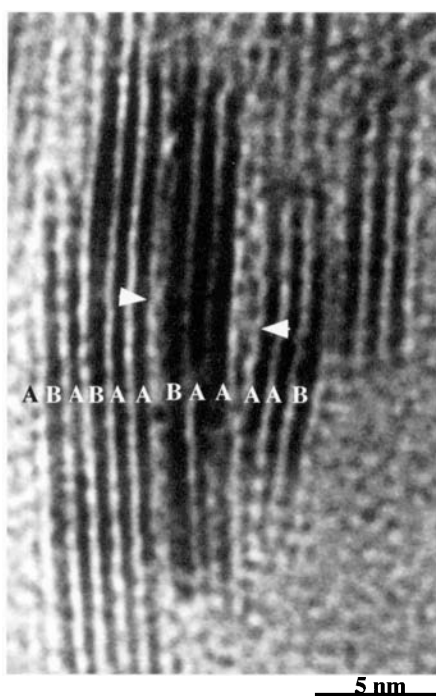
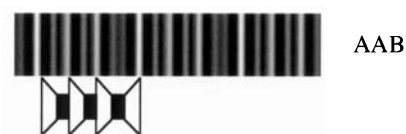


Figure 3. The lattice fringes of the sample 2 obtained by TEM. Each domain is consisting of two serpentine-part (A) and one smectite-part (B). The arrow shows a curve in a domain.

layering one by one. And the border of the interferential fringes seems to correspond to the interface of two Si-O sheets (Figure 2). In Figure 3, each particle of sample 2 has 1-2 cycled interferential fringes having 25 Å periodicity, and consisting of three black parts mostly having the thickness of 7:7:10 ratio. The image of computer simulation in Figure 4 shows that interstratified smectite/chlorite = 1/1 mineral should have the image of the lattice fringe consisting of three black parts having different ratio of thickness (about 3:2:3). Thus, the sample 2 was found to be interstratified serpentine/smectite = 2/1 compound with the domain consisting of two serpentine like-part and one smectite like-part usually layering as AAB.

In Figures 2 and 3, each domain seems to curve to the direction of the serpentine-part. It is probably due to the lateral misfit between the octahedral and tetrahedral sheets as usually

Interstratified serpentine/smectite = 2/1 compound

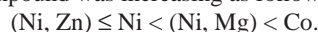


Interstratified chlorite/smectite = 1/1 mineral



Figure 4. The lattice images of interstratified serpentine/smectite = 2/1 compound and interstratified chlorite/smectite = 1/1 mineral simulated by MacHREM under the condition of defocus = 870 Å. All of them are polytypism consisting of 4 tetrahedral sheets and 3 octahedral sheets.

observed in serpentine and kaolin minerals (i.e. chrysotile, halloysite). In the structure of these 1:1 phyllosilicates, the outer curve generally consists of the larger sheet.¹ Since the Ni-OH and Mg-OH octahedral sheets are larger compared to Si-O tetrahedral sheets, the inner surface (serpentine-side) of the domains in Figures 2 and 3 should be Si-O sheet. Thus, it can be considered that each surface of the particle of the samples 1 and 2 mainly consists of the Si-O sheet. It has been known that in the 1:1 phyllosilicate group, Si-OH surface of tetrahedral sheet tends to have negative charge in the solution.¹ The high MB adsorption of the interstratified serpentine/smectite compounds² also supported their Si-O rich surfaces. According to Torii et al.,³ depending on the composition of the metals in octahedral site, the apparent viscosity of serpentine/smectite compound was increasing as follows;



From the description of these samples, the value of $d(060)$ was slightly large in Co-bearing samples ($=1.54$ Å) compared to another ($=1.53$ Å), and not only the layer charge but also the size of b-axis seemed to affect the viscosity. In Figures 2 and 3, the interferential fringes are separated in the curved parts, and the thickness of one black fringe is changing partially. Thus, these structural misfits seemed to disturb the layering and cause the partial rotation of Si-O sheets to cancel the curvature.

In conclusion, interstratified serpentine/smectite = 2/1 compound was identified by TEM for the first time as mainly consisting of AAB domain. The particles were considered to have Si-O rich surfaces, which might affect their behavior in solution.

References and Notes

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