Intercalation of Nickel Hydroxide into Large Crystal of Vermiculite

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Vermiculite of centimeter size was treated with a nickel nitrate solution under hydrothermal condition. A complex intercalated with nickel hydroxide was produced at the part within 100 μm from the edge and 10 μm from the surface under the conditions of 250 °C for 100 h. In the inner regions, nickel hydroxide was intercalated in the layers having no fixed K, but not intercalated in the region having fixed K.

Intercalation reactions involving the hydrolysis of transition metal ions that form a mono-molecular structure in the interlayer of clay minerals have been widely researched in order to design new materials with varying and unique properties.[1,2,3] Transition elements generate interesting physical properties including two-dimensional magnetic property effects.[4,5] However, fine particles of either smectites or artificial mica-like materials under 2 μm particle size have so far been mainly used as the host materials for interlayering complexes. Moreover, few reports have been published with regard to the study of the reaction process using large crystals because of their poor reactivities. In order to conduct a precise investigation of their properties or put this to practical use, a clay inorganic complex should be synthesized using a large two-dimensional crystal. We reported the synthesis of a nickel hydroxide-vermiculite complex (NHVC) by hydrothermally processing a fine vermiculite powder.[6] Vermiculite, however, can be also obtained on the order of several centimeters. If NHVC can be synthesized using vermiculite of the order of centimeters, the properties will be of wide interest, and this synthesis process will also be useful as a method of synthesizing new materials.

The starting material was vermiculite, $K_{0.47}Mg_{0.19}2.31H_2O$ $(Si_{3.03}Al_{0.96})(Mg_{2.51}Fe_{0.34}Ti_{0.05})O_{10}(OH)_2$, from Transvaal, South Africa (Nichika Co. Sample No. MU-718). It was cut with scissors into uniform
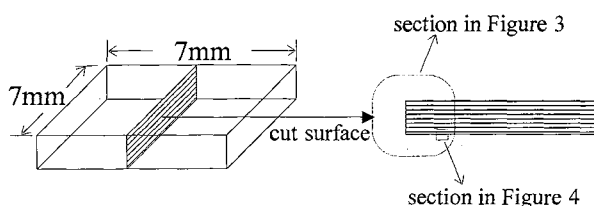

Figure 1. Sample preparation.

squares measuring 7 mm by 7 mm as shown in Figure 1. Coarse-grained vermiculite is generally formed by the weathering alteration of biotite, and K remains in its interlayer. Therefore, vermiculite generally has an interstratified structure composed of layers of 1.0 nm (A-type layer) in thickness, with K^+ in the interlayer, and layers of 1.4 nm (B-type layer) in thickness, with Mg^{2+} in the interlayer. Vermiculite used as a starting material was also a mineral having a complex interstratified structure composed of the A-type layers and B-type layers as shown in Figure 2(c). Ion-exchange reactions at room temperature clarified that 1/3 of the K^+ ions and all of the Mg^{2+} ions existed as exchangeable ions, and 2/3 of the K^+ ions existed as non-exchangeable ions. The vermiculite was placed in a 100 ml
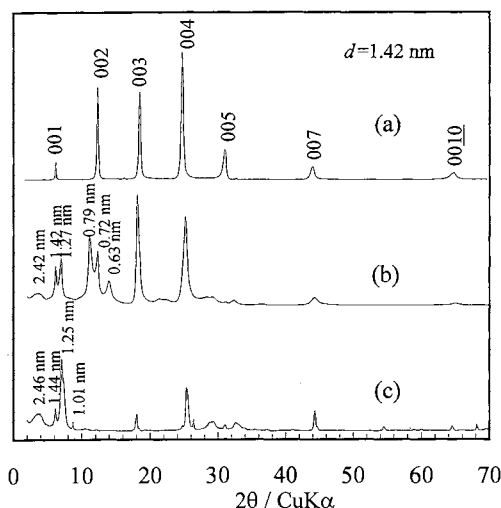

Figure 2. X-ray diffraction patterns of (a) the surface of product, (b) the cleavage face of the product, and (c) the starting material.

Teflon bottle, and 60 ml of saturated nickel nitrate solution was then added. The bottle was sealed in a Moley-type bomb and maintained for 100 and 144 h at 250 °C. The products were then separated from the solution and washed with distilled water. The untreated vermiculite is a brown crystal, while the product is totally dark green due to the intercalation of nickel hydroxide.

The sample, measured by XRD, was affixed to an aluminum holder with plasticine so that its outside would be flat. Figure 2 shows the XRD patterns of (a) the surface of the product, (b) the cleavage plane, and (c) the Transvaal vermiculite. The surface of the product shows 1.42 nm basal reflections. Its profile is similar to that of the NHVC reported by Uehara et al. (in press)[6] with regard to the relative intensities of the 00l reflections. The basal spacing of Ni^{2+}-exchanged vermiculite was reduced to 1.0 nm by treating with KCl solution. However, KCl treatment did not change the diffraction profile of the surface of the product. In addition, the content of Ni = 1.88 per half unit cell was larger than the 0.43 estimated value for the Ni^{2+}-exchanged form. These results suggest that nickel hydroxide has been almost completely intercalated into the regions close to the surface of the crystal. Hereinafter, we will abbreviate its 1.4 nm layer which is intercalated with nickel hydroxide as the C-type layer. On the other hand, the basal reflections corresponding to about 2.4 nm were observed in its cleavage plane in the inner regions. It can be seen that regular and irregular interstratified structures exist in Figure 2(b), which are composed of the 1.4 nm layer and A-type layer. No change in diffraction profile on treating with KCl solution supported the belief that this 1.4 nm layer is composed of a C-type layer into which nickel hydroxide is intercalated. This result shows that nickel hydroxide was intercalated in the entire region of the particle except for the A-type layers.
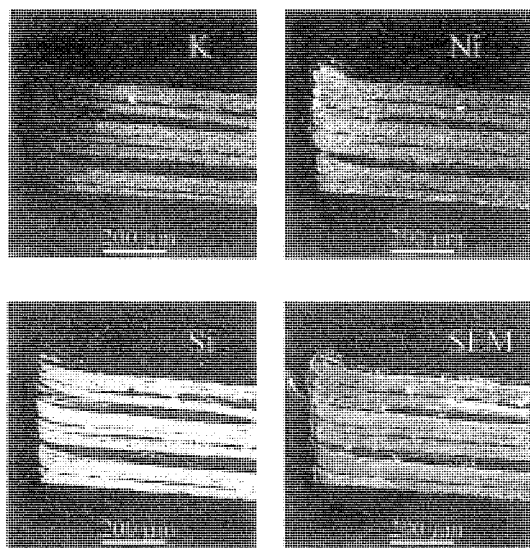
Figure 3. SEM photograph and X-ray digital maps of the area shown in Figure 1.

Figure 5. Line scan analysis at segment *se* shown in Figure 4.

The sample was prepared for the EPMA measurement by cutting a 7 mm by 7 mm square sample as shown in Figure 1. Figure 3 shows the SEM photograph and X-ray digital maps of the product synthesized in 100 h. As clearly shown in Figure 3, the distribution of Si matches the SEM image. Most of the K has been replaced by nickel hydroxide and is lost in the region extending to about 100 μm depth from the edge and about 10 μm depth from the surface of the crystal. The concentration of Ni is higher where that of K is low. As shown in Figure 4, we enlarged the area indicated by the rectangle in Figure 1 for a more detailed examination. In the SEM photograph, the lower part of segment *ab* is a partly flaked-off area, and the *ab* line is the surface line actually exposed to the $Ni(NO_3)_2$ solution. This Figure 4 shows that K has been completely leached and has been replaced by nickel hydroxide in the region extending to about 10 μm depth from the surface. This figure also shows that K and Ni are uniformly distributed in the inner regions. Figure 5 shows the result of a line scan analysis for segment *se* in Figure 4. It clearly shows that K is not present in the region extending to about 10 μm depth from the surface. The composition of nickel hydroxide per half unit cell has been estimated to be $Ni_{1.88}(OH)_{2.91}$ for this surface region. In the inner regions, however, K

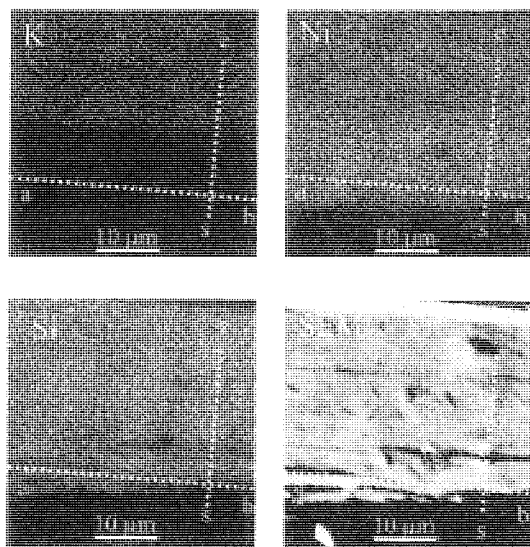remained at almost a fixed ratio, and it seemed as if an equilibrium had been apparently reached between K and nickel hydroxide ($K_{0.32}Ni_{1.31}(OH)_{2.09}$ per half unit cell). The amount of Ni which can be expected to exist as the Ni^{2+} form is estimated to be $(0.85-0.32)/2 = 0.27$. However, the amount of Ni that actually existed in these inner regions was far larger than the estimated value. Even when these regions were treated with KCl solution, there was no change in its basal spacing. Therefore, it can be considered that, also in these inner regions, nickel hydroxide was intercalated in the B-type layers, but it was not replaced in the A-type layers.

The cause of the above results is discussed as follows. Intercalation of nickel hydroxide easily occurs in the B-type layers with an open interlayer caused by retaining Mg^{2+} ions. However, it hardly occurs in the A-type layers with a closed interlayer caused by retaining K^+ ions. This is consistent with the appearance of the diffraction profile corresponding to the interstratified structure composed of C-type and A-type layers as observed in the cleavage plane in the inner regions. However, in the regions within 10 μm of the surface and 100 μm depth from the edge of crystal, nickel hydroxide was completely intercalated in the interlayer of the A-type layer. The alternation reaction of a phase having K-fixed layers accounts for this result. The alternation reaction occurs in the part of the surface and the edge contacting the acid solution. In the initial stage of the alternation reaction, K may be preferentially dissolved as reported by Kuwahara and Aoki (1995).[7] This reaction causes swelling of the interlayer portion. Consequently, it is considered that the regions within about 10 μm of the surface and 100 μm of the edge have a single phase of the intercalated structure. Based on these results, it was considered that further extension of time would also make it possible to obtain a material having a complete single phase even further into the interior of the sample. However, in the case of the product prepared at 144 h, the rate of the regions having the single phase structure could be increased slightly, although the elution of Mg^{2+} ions in an octahedral sheet began to be observed. These findings indicate that further extension of time will not be very effective for that purpose. Therefore, using vermiculite having no fixed K ion in the interlayer as a starting material will be most effective for synthesizing NHVC in which complete substitution of nickel hydroxide is achieved in the interior in a short time.

Figure 4. SEM photograph and X-ray digital maps of the area shown in Figure 1.

References and Notes
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