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# Transmission Electron Microscopic Study of Sancheong Halloysite

## 산청 할로이사이트의 투과전자현미경 연구

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**ABSTRACT:** Transmission electron microscopic study including single particle electron diffraction and morphological observation using replica and thin section was carried out for the Sancheong halloysite. Halloysite tube generally consists of inner circular and outer polygonal leaves. Primary triangular or concave voids are found between inner and outer leaves. Cross-section of halloysite tubes whose diameters are smaller than 500 Å are generally circular, whereas those larger than 500Å are polygonal. Electron diffraction pattern of thick polygonal halloysite tube shows that it has a 2-layer monoclinic structure as suggested by previous workers.

**요약:** 산청 할로이사이트의 전자 회절분석 및 레플리카와 박편을 이용한 형태 연구결과 관상 할로이사이트는 반경이 서로 다른 몇 개의 관들이 중첩되어 있으며 내부의 작은 관은 원형이나 외부의 큰 관은 다각형으로서 두 관 사이에 삼각형의 공극이 형성되어 있음이 관찰되었다. 할로이사이트의 단면은 대체로 직경이 500Å보다 작으면 원형을 이루고 그보다 크면 다각형을 이룬다. 다각형의 단면을 갖는 할로이사이트의 전자 회절상은 이들이 이층 단사 구조를 갖고 있음을 지시한다.

## INTRODUCTION

Halloysite and kaolinite are the major constituent minerals of Sancheong kaolin which has been formed by the weathering of anorthosite (Jeong, 1987; Jeong and Kim, 1989). Individual kaolinite particle is easily observed under optical microscope as well as scanning electron microscope because of its large size. It is characterized by vermiform books of various origin. However, detailed morphological and structural characteristics of halloysite have not been studied. Transmission electron microscopic(TEM) study shows that the Sancheong halloysites dispersed on the collodion substrate have tubular forms. But, the general alignment of tube axis vertical to the electron beam makes it difficult to study the internal and external details of individual halloysite particles. X-ray diffraction patterns of the oriented halloysite specimen (Sang, 1980; Jeong and Kim, 1989) show a remarkable enhancement of basal reflections with simultaneous weakening of hk-diffraction bands, implying that halloysite is not a completely round tube. Furthermore, it is known from previous electron diffraction studies that halloysite has a unique 2-layer periodicity distinct from kaolinite (Honjo and Mihama, 1954; Chukhrov and Zvyagin, 1967).

Present paper concerns the study of the detailed internal and external morphology and structure of Sancheong halloysite for the specimens prepared by dispersion, replication, and ion thining technique.

## EXPERIMENTAL

The kaolin samples for the present study consist of halloysite and kaolinite with minor vermiculite and plagioclase. Halloysite was separated by centrifugation, and the purity was checked by X-


**Fig. 1.** TEM photograph and diffraction patterns of halloysite. (A) Tubular morphology of halloysite (arrow) with internal tunnel. (B) Electron diffraction pattern of polygonal halloysite tube (arrow in (A)) showing intense{021} spots. (C) Streaky electron diffraction pattern of circular halloysite tube. (Scale bar=0.1$\mu$m)

ray diffraction. Halloysite particles in aqueous suspension were loaded on the carbon-coated collodion substrate. Replica was prepared for halloysite film deposited on the mica plate by platinum shadowing at 40° and subsequent carbon backing. The clay film and replica were floated off the mica plate onto the distilled water, and subsequently treated with 40% HF solution to dissolve halloysite. The replica was loaded on copper grit for TEM observation. Thin section was prepared by argon ion-thinning for the undisturbed bulk specimens fixed by Araldite epoxy resin. Therefore, photographs obtained from ion-thinned specimen represent the natural texture of halloysite in kaolin with no artificial treatment except dehydration. JEOL JEM 200CX instrument operating at 160 kV in the Material Testing Center of Seoul National Uiniversity was used.

## RESULTS

TEM photograph of the specimen loaded on the collodion substrate shows a typical elongate form of halloysite with tunnel (Fig.1A). The diameter of tube is about 0.1$\mu$m with various length. Single particle electron diffraction pattern of halloysite tube (Fig.1B) shows more or less ordered arrangement of discrete spots which are indexed on the base of 2-layer monoclinic cell as already suggested by Honjo and Mihama(1954), Chukhrov and Zvyagin(1967), and Kohyama et al(1978). The tube is oriented to b-axis. But the other tube shows streaky diffraction pattern (Fig. 1C) and does not give such ordered and discrete electron diffraction spots implying structural disorder.

TEM photographs of replica (Fig.2A, 2B, and 2C) show external features of halloysite particles. Some thick elongate halloysite particles are not completely cylindrical tube but polygonal one as shown in the angular ridge(arrow 1 in Fig.2A), but the polygonal form is not common to all the particles. The ends of the halloysite tube generally split into several terminating twigs(arrow 2 in Fig.2A). Zigzag-shaped growth edges parallel to the tube axis are found on the tube(Fig.2B). Parallel growth of halloysite tubes is often found(Fig. 2C).

Four different TEM micrographs of thin section (Fig. 3A, 3B, 3C, and 3D) show cross-sections of individual halloysite tubes. The diameter of the halloysite tube in the Figures ranges from 600

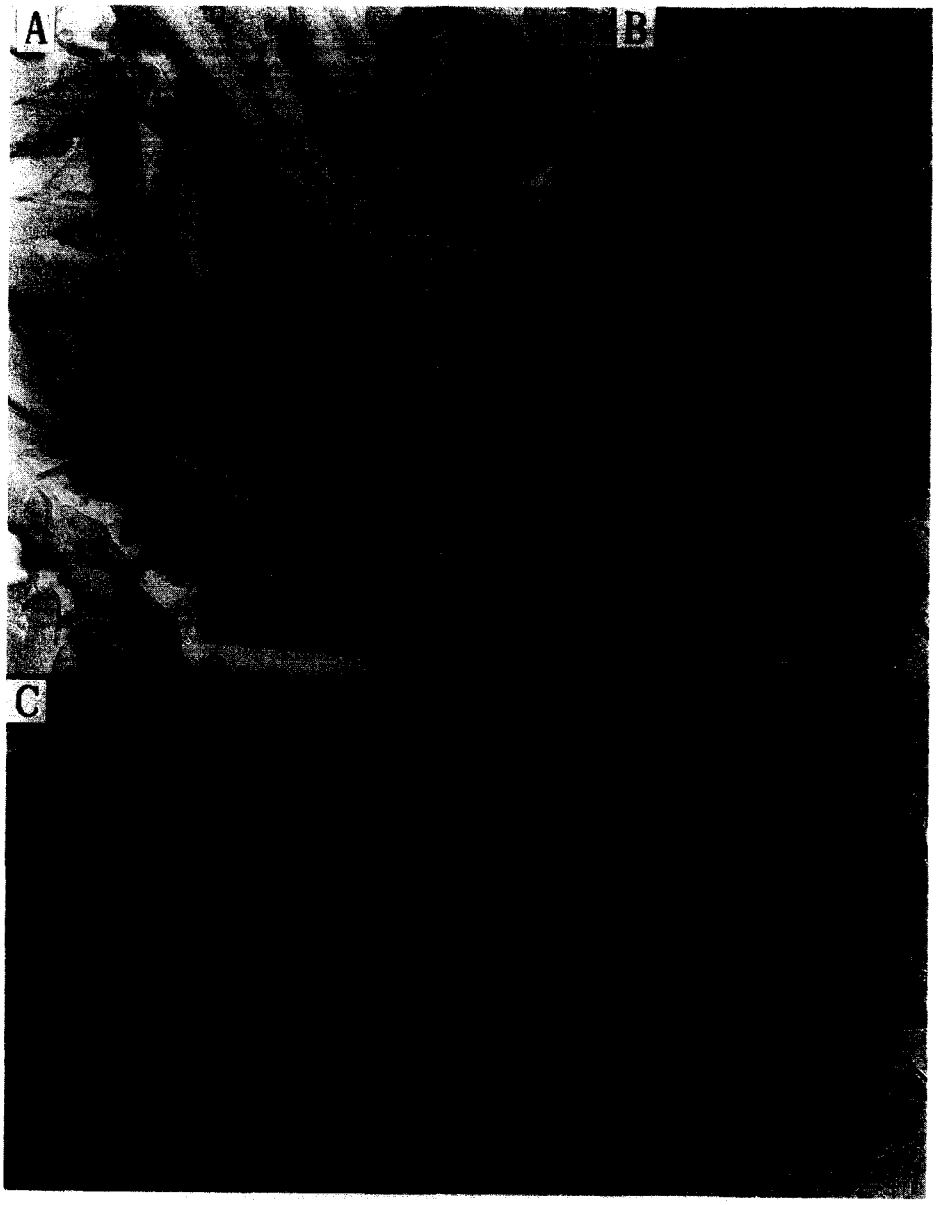


**Fig. 2.** TEM photographs of replica of halloysite tube. (A) Polygonal form of halloysite tube(arrow 1) and splitting of tube into several twigs at the end(arrow 2). (B) Zigzag-shaped growth edges (arrow) on the tube parallel to the tube axis. (C) Parallel growth of two halloysite tubes arrow. (Scale bar = 0.2$\mu$m)

Å to 1700 Å, and the thickness of halloysite leaf ranges from 110Å to 290Å which is equivalent to 15~40 layers if one layer thickness of halloysite is taken to be 7.3Å. The thick halloysite tube shows the concentric structure that two or three halloysite leaves are aligned in a concentric pattern. Inner leaf of a small radius has a circular form, whereas outer leaf of a larger radius has a quadrilateral or pentagonal form. Triangular voids are formed between circular inner leaf and

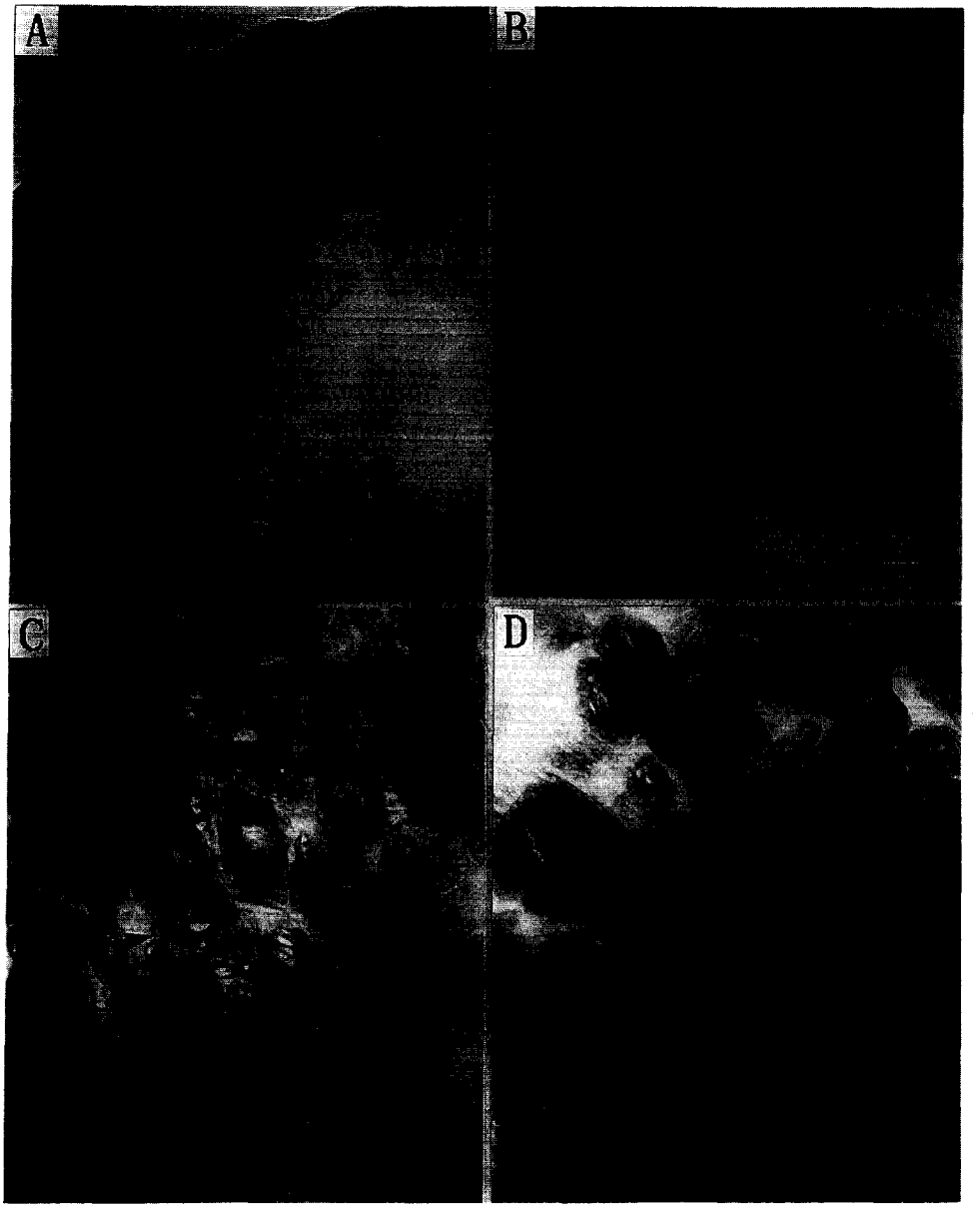


**Fig. 3.** TEM photographs of thin section of halloysite tube. (A) Circular cross-section of small tube(arrow 1) and quadrilateral cross-section of large tube(arrow 2) with triangular voids. (B), (C), (D) Polygonal halloysites and triangular voids. White spots in the photographs were formed by electron beam damage. (Scale bar = 0.1 $\mu$m)

polygonal outer leaf. The present study shows that cross-sections of halloysite tubes whose diameters are smaller than 500 Å, are circular, whereas those larger than 500 Å are polygonal. Therefore, roundness of the tube is correlated with the radius of the tube.

## DISCUSSION

Electron diffraction study shows that halloysite has a 2-layer monoclinic structure as suggested by previous workers(Honjo and Mihama, 1954; Chukhrov and Zvyagin, 1967; Kohyama et al., 1978). TEM photographs of replica and thin section show that halloysite tube has a variable morphology in cross-section from circular to polygonal. Polygonal morphology of halloysite was previously recognized by TEM study on replica (Chukhrov and Zvyagin, 1967), replica and thin section (Dixon and McKee, 1974), and thin section (Robertson and Eggleton, 1991). Robertson and Eggleton (1991) asserted that some part of the tube showing mottled contrast may be kaolinite. Mottled contrast was not observed in this study and XRD pattern of the sample showed mostly halloysite (10Å) diffraction pattern. Therefore, the tubes in the photographs are halloysites. Ordered and discrete difffraction spots obtained by Chukhrov and Zvyagin (1967) were apparently obtained from the thick polygonal tubes, whereas streaky diffraction spots obtained by Kohyama et al. (1978) might from the cylindrical tubes. Each plate of polygonal tube has a more ordered structure than cylindrical tube which has structural disorder originating from curved lattice. Photograph of thin section shows that thick halloysite crystal has a concentric structure consisting of inner circular and outer polygonal leaves. The discrete diffraction spots in this study arise from the plate of outer polygonal leaf of thick halloysite tube. Thin circular tubes show no diffraction pattern or streaky diffraction pattern implying a high stuctural disorder. Therefore, there is a heterogeneity in the crystallinity of halloysite. Although X-ray diffraction patterns do not show any splitting in (02, 11) diffuse band implying complete disorder(Jeong and Kim, 1989), TEM study shows that some halloysite of polygonal form have a high structural order of 2-layer periodicity.

Some circular voids might be formed by the dehydration as suggested by Kohyama et al. (1978) who observed the formation of circular voids during the dehydration, but triangular voids might be primary structure due to non-harmonic geometric setting of inner circular and outer polygonal leaves. Enhancement of basal reflection observed in the X-ray diffraction pattern of oriented halloysite film(Sang, 1980; Jeong and Kim, 1989) is apparently caused by the polygonal morphology of halloysite tube.

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