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Internal structure analysis of mica particles coated with metal oxide by transmission electron microscopy

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Abstract

The morphology and internal structure of mica particles coated with metal oxide, TiO_2, produced by the hydrolysis method were investigated by transmission electron microscopy on thin sections prepared by means of a specially designed sample preparation technique. Cross-sectional TEM images clearly revealed the comparatively uniform thickness and composition of the TiO_2 layer as a component of the particles. It was found that the TiO_2 layer was composed of randomly oriented small particles about 50 nm in diameter with small variation of the diameter depending on the position in a mica particle, while near the surface of the mica particle a monolayer of TiO_2 oxide was observed.

Keywords: TiO_2/mica particle; Pigment; Thin section; Thickness; Internal structure; Transmission electron microscopy

1. Introduction

Recently, intensive work to prepare oxide layers uniform in thickness, size, and composition on particle substrate has been initiated for the purpose of producing advanced materials in the field of the automobile industry. For instance, intensively colored pigments based on mica particles coated with colored metal oxides have successfully been studied by using homogeneous hydrolysis of metal sulphates and modified versions for highly condensed systems [1–4]. One of the most important applications of mica is pearlescent pigments in the field of the automobile industry [5,6], which consist of mica powders coated with a thin layer of metal oxide, mostly TiO_2. The presence of a highly refractive layer covering the less refractive support material results in a significant pearlescent effect and provides colors resulting from optical interference [7–15]. However, one difficulty which arises from the hydrolysis process is the realization of uniform thickness and fine grain of the oxide layer on the mica. This is crucial for high performance pearlescent pigments. In particular, the color performance of pigments in car paint is known to depend strongly on the thickness and composition of the oxide layer. In order to obtain optimum pearlescent pigment performance, thickness control and a fine structure of the metal oxide are absolutely necessary. Transmission electron microscopy (TEM) combined with a new sample preparation technique using ion milling proved quite useful for detailed characterization of the internal structure of mica particles coated with colored oxides. Detailed information on internal structure provided us with many clues for understanding layer formation on the mica. Most recently, mica particles coated with TiO_2 metal

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oxide were produced by concentrated homogeneous hydrolysis of metal sulphates with urea in the presence of mica particles. By X-ray diffractometry (not shown), the crystal structure was identified as anatase, close inspection of the internal structure of these mica particles coated with TiO_2 metal oxide seems to be needed for a complete understanding of their characteristic growth mechanism. For this purpose, we have attempted direct observation of the internal structure. This article is a short report on a study by TEM coupled with a new sample preparation technique with ion milling of the internal structure of mica particles coated with TiO_2 metal oxide prepared from a condensed homogeneous hydrolysis system.

2. Experimental

Samples of mica particles coated with metal oxide were prepared by the standard procedure of the hydrolysis method [16]. Thin sections for TEM were prepared with a specially designed sample preparation technique with ion milling as shown in Fig. 1. Although thin sections of some particles like a hematite, are obtained by an ultramicrotomy technique [17] without damage, it is very difficult to obtain optimum TEM samples in the case of weak bonding between particle substrate and coating layer in the case of such mica particles coated with metal oxide. Thus, the specimens for TEM were prepared by techniques including mechanical polishing, dimpling, and Ar^+ ion milling after mixing of epoxy and powders in curing. No resulting mechanical damage to the cross-sectional TEM specimens can be found in micrographs of the samples. The internal structure was investigated through cross-sectional TEM observations by using a JEOL 2010EX TEM operated at 200 kV. Energy dispersive X-ray analysis was applied to the oxide layer area by a JEOL 2010EX equipped with an Oxford instrument.

3. Results and discussion

Fig. 2(a) shows a SEM micrograph of mica coated with TiO_2 metal oxide in this study. Fig. 2(b) shows an enlarged image of the top surface of a muscovite mica particle, corresponding to the white rectangular region in Fig. 2(a). The TiO_2 layers are composed of small particles, approximately 50 nm in diameter, and bound by rough surfaces with small bumps, as shown in Fig. 2(b). It can be seen that the layer of anatase consists of well-distinguished homogeneous nano particles, with no signs of peeling. Fig. 3 shows a cross-sectional bright-field image of the mica coated with TiO_2 metal oxide.

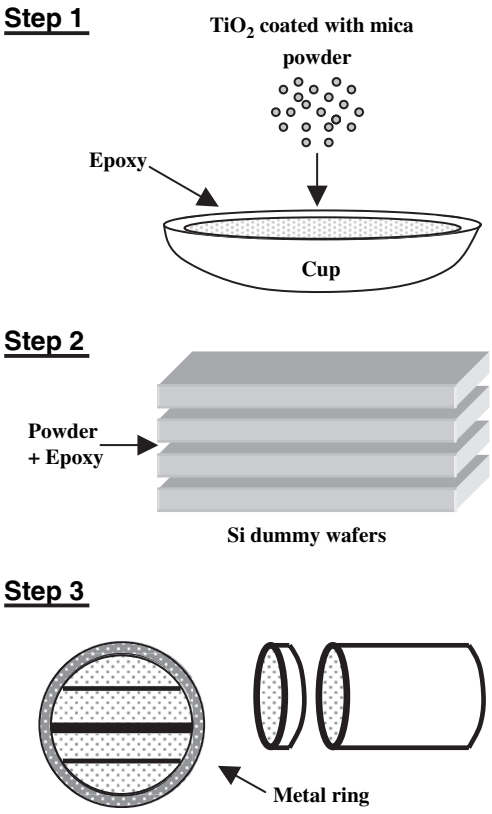

Fig. 1. A schematic diagram showing how TEM specimen preparation techniques for particles coated with metal oxide layer in this study.

The thicknesses of the mica particles and TiO_2 metal oxide layers were estimated to be ~60/50 nm, respectively. Clearly, the muscovite particle bears a uniform oxide layer and the TiO_2 metal oxide surface layer can be distinguished from the mica substrate. No interfacial layer between the mica and the oxide layer was observed. It was found that the metal oxide layer was composed of randomly oriented small particles, with small variation of the diameter depending on the position in a mica particle, while a monolayer of TiO_2 oxide was observed at the surface of the mica particle. No significant amounts of metal oxides precipitated outside the mica surface were observed. The inset of Fig. 3 is a corresponding selected area diffraction (SAD) pattern obtained from the interface region of the oxide layer and mica with the incident beam parallel to the $[11\underline{2}0]_{mica}$ direction. The SAD pattern clearly shows that the oxide layers are polycrystalline. Fig. 4 shows high-resolution TEM images of a thin section. From the lattice images of Fig. 4, the TiO_2 layers are identified as anatase, in agreement with the results from X-ray diffractometry. Furthermore, it is clearly observed that the high probability of such images may suggest an inherent property of the TiO_2 crystal inhibiting epitaxial growth, which may be relevant to the formation of the

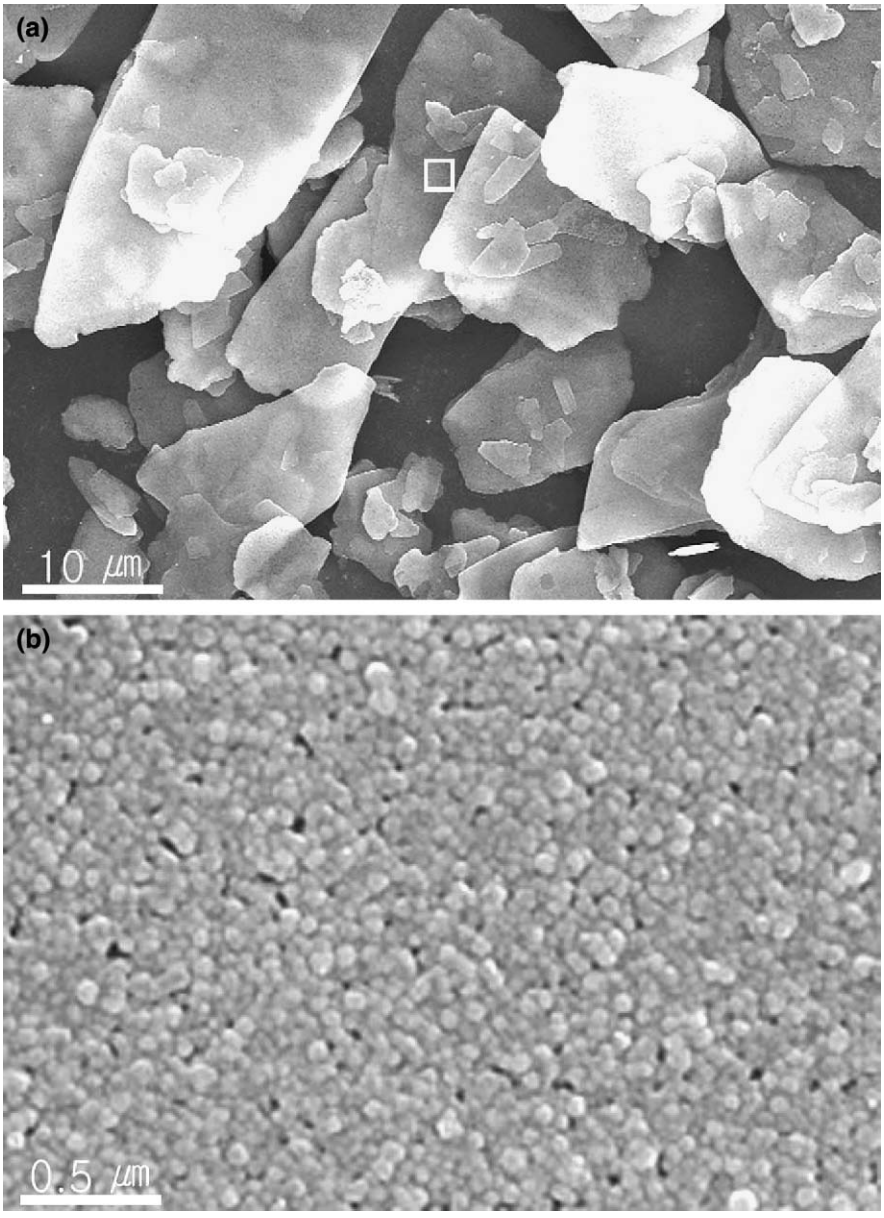

Fig. 2. (a) Plan-view scanning electron micrograph of the mica particles. (b) Enlarged SEM image, corresponding to the white rectangular region in (a).

polycrystalline structure consisting of the small sub-crystals. Fig. 5 shows EDX spectra obtained from the thin sections of TiO_2 layer. From quantitative analysis of EDX spectra from the sections of TiO_2 layer, it was found that the atomic ratio of Ti to O was about 1:2, although there were some variations in the ratio depending on the analyzed positions in the sections. This result strongly supports the contention that the optical interference effect of the pigments derived from the homogeneous hydrolysis method was dependent on the thickness of the oxide layer and subsequent thermal treatment.

4. Conclusions

A new sample preparation technique using ion milling can be very useful for internal structure analysis of mica particles coated with a TiO_2 metal oxide layer. Cross-sectional TEM images clearly revealed the uniform thickness (about 50 nm) and composition of the oxide layer. It was found that the metal oxide layer was composed of randomly oriented small particles with small variation of the diameter, while a TiO_2 oxide monolayer was observed at the surface of the mica particle.

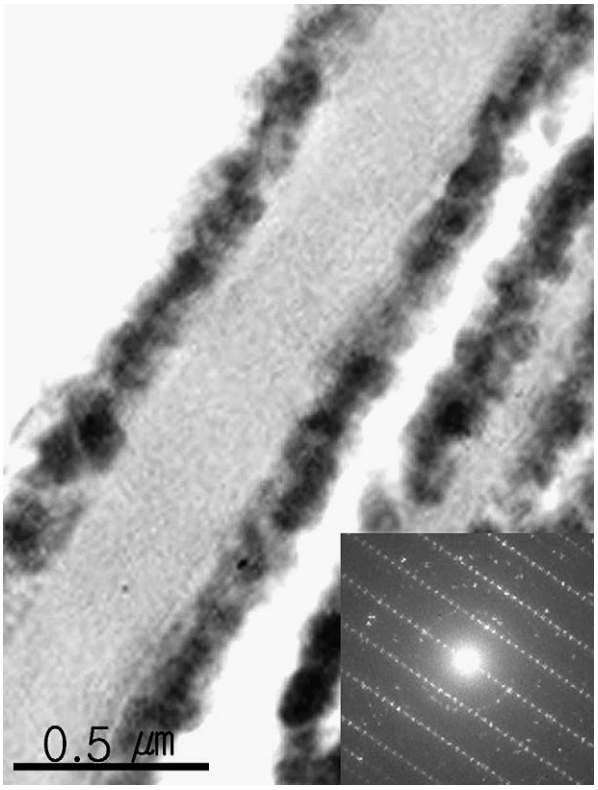

Fig. 3. Cross-sectional TEM image of the mica coated with TiO_2 metal oxide. The inset of Fig. 3 is a corresponding selected area diffraction (SAD) pattern obtained from the interface region.

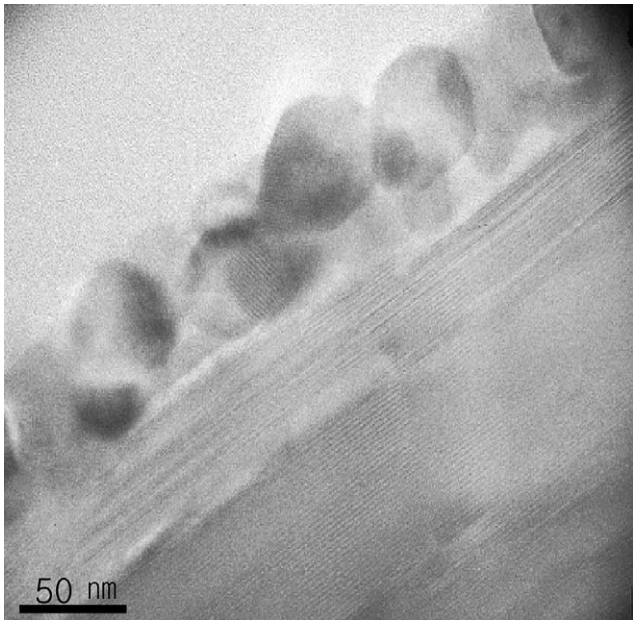

Fig. 4. Cross-sectional lattice image of the mica coated with TiO_2 metal oxide.

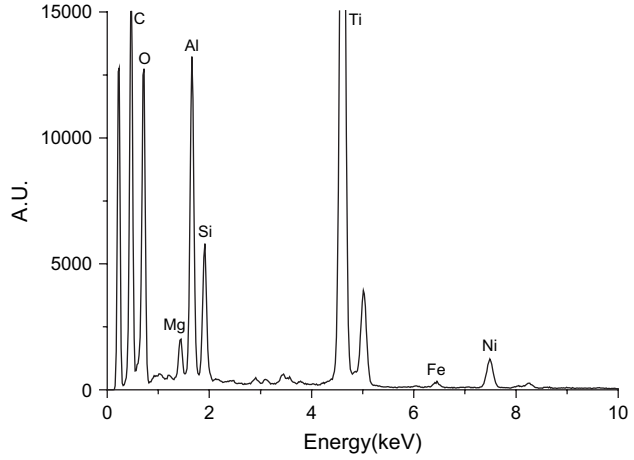

Fig. 5. EDX spectra obtained from sections of the TiO_2 metal oxide layer.

Acknowledgments

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