In-situ Observation on Oxidative Process of Calcium Ultrafine Particles Using Specimen Transfer System in TEM

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Calcium oxide particles produced by burning calcium in air was the cubic shape as well as MgO particle formation. Since metallic calcium was the most active substance in air or oxygen gas, the pure calcium particles could not obtain. In ordinary specimen preparation techniques for conventional transmission electron microscopy (TEM), the specimens are prepared outside the microscope and transferred to the specimen stage with exposed in air. Therefore, the oxidation effect on the calcium in nm-sized particles was inevitable for the grain observation process.

In order to observe as-prepared structure of cluster, ultrafine particles and dust particles prepared in laboratory, the specimen transfer chamber for TEM has been constructed to observe structure of cluster on metallic nanoparticles substrate (K. Ishiyama et al., 1985). In the present study, the specimen transfer holder for the TEM has been newly designed for a side-entry-type of H-9000NAR TEM for in-situ observation.

Structure of calcium particles produced in inert gas and the oxidative process of calcium particles has been examined by the in-situ method. The metallic calcium is bcc structure above 740 K, and the stable phase at room temperature is fcc structure. The particle was produced by heating tungsten boat at 1081 K in an inert gas. Vapor pressure of calcium becomes about 1 Torr which is the typical grain formation condition in laboratory (R. Ueda, 1987). Most of the produced calcium particles were fcc structure with the defect in a particle. The external shape of the particles was explained by the rhombic dodecahedron which was the stable metallic particle shape of bcc structure. Therefore, the bcc particles were produced near the heater and transformed to the fcc structure keeping the external feature. As indicated the iron particle is one of the habits special to fcc despite the crystal structure is bcc (Y. Fukano, 1976), the defects on the transformation were predominantly produced in a calcium grain.

The surface of calcium particles with the size of 300 nm was covered with oxide layer by the topotactic relation with the thickness of 10 nm order. These particles were stable in air; oxidation progressed very slowly. When the calcium particles size were 10 nm order, the particles were changed CaO with cubic shape. Since the oxidative energy of calcium is very high, Gibbs free energy of calcium formation is highest among metals, Ca nanoparticles easily burned in atmosphere contained oxygen.