ANISOTOPIC EVAPORATION AND CONDENSATION OF CIRCUMSTELLAR CORUNDUM. A. Takigawa[1], S. Tachibana[1], H. Nagahara[1], and K. Ozawa[1], [1]Dept. of Earth & Planetary Sci., Univ. Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan. takigawa@eps.s.u-tokyo.ac.jp

Introduction: In circumstellar environments such as extended atmospheres around AGB stars or protoplanetary disks, solid dust particles condense from high temperature gas. Equilibrium condensation models predict that corundum (Al_2O_3) is one of the first condensates from gas of the solar composition [e.g., 1-3], and it is thus an important mineral that can potentially record the onset of dust formation process in circumstellar environments. Corundum belongs to the trigonal crystal system, and it shows anisotropy in various properties such as permittivity, thermal expansion and elasticity. Growth of anisotropic crystals also often undergoes anisotropically and results in formation of crystals with a specific crystallographically anisotropic shape (e.g., [4]). In other words, a crystallographically anisotropic shape of mineral records the formation process and/or condition of the mineral.

The processes responsible for dust evolution in space are condensation and evaporation of solid. Because physical and chemical conditions of dust-forming environments change with time owing to various processes such as the expansion of atmosphere around evolved stars or the evolution of protoplanetary disks, it is important to understand kinetics of dust evolution processes. In this study, we conducted evaporation and condensation experiments of corundum in order to obtain the anisotropic evaporation and condensation rates quantitatively and understand the dust formation condition in circumstellar environments.

Evaporation & Condensation Experiments: Three rectangular single crystals of corundum (3-5 x 10 x 0.5 mm^3), of which largest surfaces were {0, 0, 0, 1}, {1, 1, -2, 0}, and {1, -1, 0, 0} planes (sample C, sample A, and sample M, respectively), were prepared for evaporation and condensation experiments of corundum. The <0001>* and <11-20>* orientations of corundum correspond to the crystallographic c- and a-axes, respectively. The <1-100>* direction, which is perpendicular to the plane containing the a- and c-axes, called m-planes, is referred to as the m-axis hereafter.

Evaporation experiments were conducted in a vacuum chamber made of stainless steel with a tungsten mesh heater. Samples C, A, and M were put in the furnace together in each experiment. After the chamber was evacuated to ~10^{-5} Pa by a turbo-molecular pump and a rotary pump, the samples were pre-evacuated at 500°C for 1-12 hr, heated at ~200°C hr^{-1} to 200°C below the experimental temperature, and then heated at ~20°C min^{-1} to the desired temperature of 1598, 1677, or 1787°C. Samples were heated for duration ranging from 24 to 200 hrs, and then rapidly cooled by turning off the heater.

Condensation experiments were conducted in another vacuum chamber with a tungsten mesh heater. The chamber was evacuated to high vacuum (~10^{-5} Pa) and a pellet made of alumina powder (11.5 mmϕ x 5 mmL) was put at the bottom of an iridium crucible (15 mmϕ x 40 mmL) as a gas source. The weight of the pellet was measured before and after each experiment to obtain the evaporation flux from the pellet. Samples C, A, and M were used as substrates for condensation. In each experiment, one or a few corundum substrates were put on an Ir pedestal set at 40 mm from the bottom of the crucible, where the temperature was lower than that of the gas source. The Ir crucible containing the gas source and substrates was put in the chamber and pre-evacuated at 500°C and heated at a constant rate of 20°Cmin^{-1} to each experimental temperature. The temperatures of the gas source (T_{gas}) and the substrates (T_{sbst}) were 1705°C and 1575°C, respectively.

Although mean free paths of gas species under the present experimental conditions are much longer than the size of the crucible, the gas molecules from the pellet collide the wall of crucible and hit the side and rear surfaces of the substrates in addition to the front surfaces and could condense on these surfaces. In order to evaluate the contribution of condensation on the side and rear surfaces of substrate, corundum tips with various surface areas (1-10 x 10 x 0.5 mm^3) were used.

After the experiments, weight changes of samples were measured by a microbalance (± 1 μg), and the surface structures after evaporation and condensation were observed with FE-SEM (JEOL JSM-7000F), and their compositions and crystallographic orientations were determined with energy-dispersive X-ray spectroscopy and electron back-scattered diffraction.

Results and Discussion:

Evaporation experiments: No residual material was found on corundum surfaces after evaporation in all the runs, showing that corundum evaporates congruently as predicted thermodynamically. Because of its refractory nature, the evaporated fraction of corundum was at most a few % in the present experiments. Such a small fraction of evaporation could be affected by the initial surface condition. However, the surfaces of starting crystals, which had been mechanochemically polished before the experiments, were very flat (±<0.5nm) and were not destroyed. Moreover, the weight losses of the samples increased linearly with heating duration at all the conditions, and the regression lines go through the origin. Thus, the small evaporation fraction of corundum has not affected the estimation of the evaporation rates in this study.

Evaporation rates along the c-, a-, and m-axes (V_c, V_a, and V_m) were calculated from the weight losses and the original shapes of the three starting samples [4, 5]. The evaporation rate along the m-axis is largest and that along the c-axis is smallest at 1600-1790°C ($V_m >> V_a > V_c$). The ratios of V_m/V_a and V_c/V_a are about 2.2 and 0.66, respectively. The evaporation coefficients of corundum, the parameter showing the degree of deviation from the ideal evaporation rate due to kinetic hindrances, are ranges 0.1-0.01.

Condensation experiments: The weight gain of each substrate divided by the effective front surface area (c-, a-, and m-substrates) increased almost linearly with time. The effective front surface areas (S_{front}) of substrates are those facing to the gas source except for the areas covered with the pedestal. The weight gains of substrates of samples M are largest, and the weight gains of samples C are slightly smaller than those of samples A. The weight gains of substrates per unit S_{front} and unit time have no correlation with the proportion of side surface area (S_{side}) to the total surface area ($S_{front}+S_{side}$). This clearly suggests that condensation on the side surfaces of substrates did not contribute to the overall weight gains, and thus the differences in weight gains of samples M, C, and A represent different condensation efficiencies on different crystallographic surfaces, i.e., anisotropy in condensation.

The obtained condensation rates along the c-, a-, and m-axes are 0.49±0.01 x 10^{-7}, 0.62±0.01 x 10^{-7}, and 1.42±0.01 x 10^{-7} g/cm^{2}s, respectively. The condensation rates along the c-, and a-axes are ~0.3 and ~0.4 times smaller than the fastest rate along the m-axis.

In order to determine the supersaturation ratio of condensation, the flux of the gas molecules hitting the substrates was evaluated. Because the crucible has a conductance for gaseous molecular flow and the substrates and the Ir pedestal could have behaved as partial lids of the crucible, the crucible could be regarded as a non-ideal Knudsen cell [6] to produce partial pressure of Al- and O-bearing gas molecules inside. The flux of Al atoms hitting the substrates (u) is calculated to be 2.0 x 10^{-7} g/cm^{2}s using the conductance of the crucible, the evaporation flux of the gas source, an equilibrium vapor pressure of corundum at T_{gas}, the evaporation coefficients of corundum, and the actual condensation flux onto the substrates. The supersaturation ratio on the front surface of the substrates (S) is given by the ratio between u and the equilibrium vapor pressure of Al for corundum at T_{sbst}, and the S in the present experiments is estimated to be ~5. The condensation coefficient of corundum under the present experimental condition is <0.1.

Mass absorption coefficients of condensed corundum: The evaporation and condensation experiments of corundum indicates that corundum formation processes proceed anisotropically in circumstellar environments, which further suggests that the morphology of circumstellar corundum could be observed spectroscopically as in the case of forsterite [4]. We thus calculated the mass absorption coefficients of corundum ellipsoids with various aspect ratios [7] using the optical constants of [8] and [9].

The shape difference of corundum was found to be distinguished with the peak positions and their relative intensities in the 10 μm band. The peak position of 13 μm feature, commonly observed from O-rich AGB stars, is well reproduced by corundum ellipsoid slightly flattened along the c-axis (r_c/r_a ~0.7), which is consistent with the aspect ratio of corundum condensates expected from the present experiments (r_c/r_a ~0.79). The width of the observed 13 μm peak is also well reproduced if there are some shape variations around r_c/r_a of ~0.79, a grain size is ~1 μm, or a thin coating of amorphous alumina is present on a corundum grain. If the condensed corundum grains re-evaporate by high-temperature thermal events, the aspect ratio of the grains could approach to unity by ~75 % of evaporation and exceed unity by further evaporation. However, the outflow from the evolved star is basically a monotonically cooling system, and re-evaporation is hardly expected to change the morphology of condensed corundum except for episodic high-temperature heating events such as propagation of shockwaves. These results strongly suggest that the carrier of the observed 13 μm peak is corundum condensates.

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