

Water Vapor in Closed-Cell *In Situ* Gas Reactions: Initial Experiments

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Modern technology for *in situ* closed-cell gas-flow allows reactions to be conducted at elevated temperatures and at gas pressures up to one atmosphere [1]. However, introducing water vapor into the cell at percentages above the ~2% possible with room-temperature air at 100% relative humidity (e.g. to mimic bench-top reaction conditions) remains challenging due to the impracticality of heating the gas feed lines into the cell that is necessary to prevent water condensation. Water-vapor experiments are being performed using as a trial specimen MgO nanoparticles (from burning MgO ribbon and collecting the smoke). MgO is a hygroscopic mineral that converts to Mg(OH)₂ (brucite) when exposed to water. Because the MgO smoke nanoparticles form perfect cubes, it was hypothesized that they could serve as a sensitive indicator for the presence of water vapor in the closed-cell gas-reactor holder. *In situ* results will ultimately be correlated to similar experiments performed in an *ex situ* reactor to confirm the presence of H₂O vapor in the cell. Results of preliminary experiments are described here.

MgO smoke particles were collected on a Protochips E-chip heater, where the chip was masked to isolate the heater membrane such that MgO particles deposited only on the heater surface. Figure 1 shows typical MgO cubes deposited on the thin (30 nm) silicon nitride membrane. Temperature effects on the stability of the MgO crystals were initially investigated by heating the E-chip with MgO deposited on it in the column vacuum to 1000°C at 5°C/s. The MgO crystals were extremely stable under vacuum heating; coarsening of the crystals initiated only at 950°C. The MgO crystals were then heated in lab air at ~50% RH (i.e. ~1% H₂O vapor at atmospheric pressure); there was no discernible difference between heating in vacuum and in lab air. The crystals in lab air were stable up to 950°C.

For the *ex situ* experiments, a special-built reactor fitted with a port to hold the JEOL specimen rod was used, and was wrapped with heating tape to prevent water condensation. Water was injected (with dry air as a carrier gas) into the chamber at 9 ml/hr, which allowed ~48% water vapor with a gas flow of 500 mL/min, while introduction of 10% of water vapor required 200 mL/min gas flow. The internal temperature was monitored by a thermocouple placed in the center of the reaction chamber; calculations indicated that heating to 85°C would preclude moisture condensation on the chamber wall and the holder.

In the first experiment, a 48% H₂O vapor condition was attempted, but it was noted that water droplets did in fact condense on the walls of the *ex situ* reaction chamber and the heater holder tip (likely due to insufficient time for equilibrium temperature to be reached before injecting the vapor). Therefore, MgO crystals were exposed to both water vapor and water for ~1 min. without applying E-chip heating. This was fortuitous, because examination of the MgO crystals clearly showed formation of the brucite outer oxide layer having an irregular, spiky-type morphology and a thickness of ~5 nm (Figure 2). The question to ask was if the spiky-type oxide layer would also form with only water vapor present, which was explored by exposing a new chip with MgO smoke cubes to flowing lab air with 10% H₂O vapor at 700°C for 30 min. in a separate bench-top furnace system. As shown in Figure 3, the MgO cubes showed that a thin amorphous layer was formed, and that the sharp cube corners became more rounded. No increased sintering of MgO crystals was observed; however, it was subsequently noted that brucite

dissociates at elevated temperatures, and a new experiment at e.g. 200°C would be a better test. This experiment, and others planned, are required to better determine whether MgO crystals can be a good indicator for *in situ* closed-cell gas-reaction with water vapor experiments, or if an alternative material should be used [4].

References:

[1] L F Allard, *et al.*, Microsc. Microanal. **18** (2012), p. 656.

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[3] K A Unocic *et al.*, *Oxid. Metals on line* (2017) p.1.

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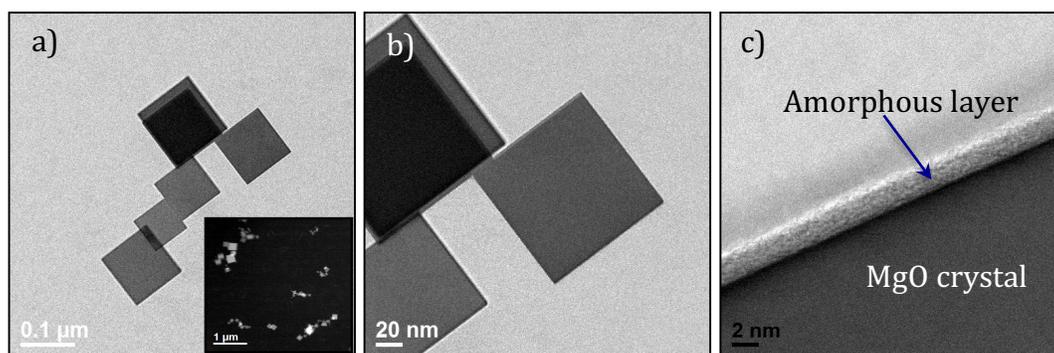


Figure 1. BF-STEM images of MgO crystals, after smoke deposition on electron transparent SiN region of Protochips E-chip. Crystals are perfectly faceted with cube morphology, and have sharp corners.

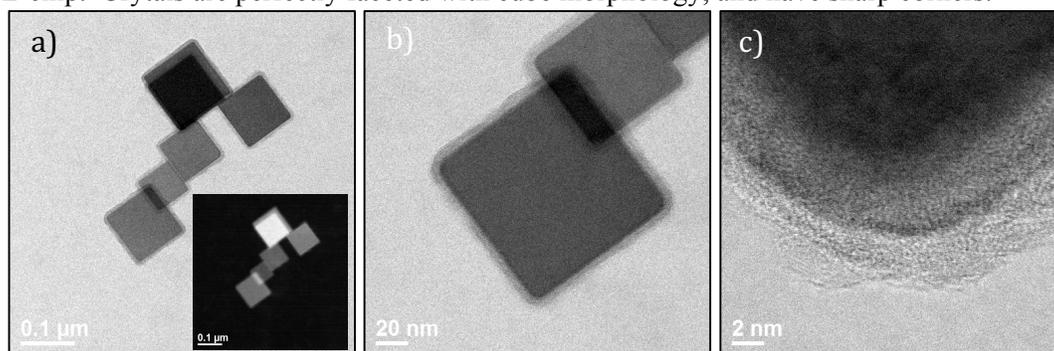


Figure 2. BF-STEM images of MgO crystals, area of Fig. 1, after *ex situ* water and water vapor 1 minute exposure at 85°C. Sharp corners became rounded, and the surface converted to a 5-6nm spikey film.

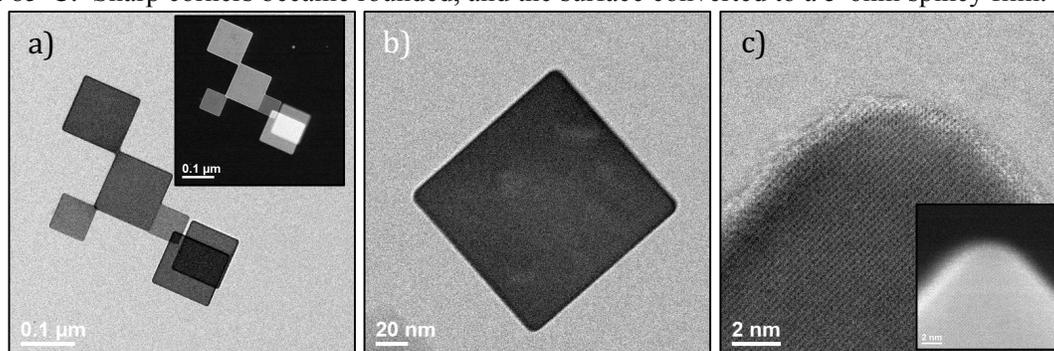


Figure 3. BF-STEM images of MgO crystals, after lab *ex situ* exposure (700°C/0.5h lab Air+10%H₂O) on electron transparent SiN. Crystals remained perfectly faceted, but the corners of the MgO crystals became rounded instead of sharp.