

EX-SITU TEM SULFIDATION STUDY OF SUPPORTED COPPER PARTICLES

C.E. Kliewer, S.L. Soled, S. Miseo, and W.R. Kliewer
ExxonMobil Research & Eng., 2545 Route 22 East, Annandale, NJ 08801

It is well accepted that environmental parameters (e.g., temperature, pressure, etc.) affect materials' properties.¹ Thus, environmentally relevant characterization conditions continue to be critical to TEM-based studies.¹ To this end, both *in-situ*¹⁻⁴ and *ex-situ*⁵⁻⁷ TEM-based protocols have been developed.

However, certain processes occur in highly corrosive (sulfur-containing) environments, and it is often not desirable to flow such gas mixtures into the TEM for *in-situ* studies or even through an *ex-situ* system due to contamination issues. Consequently, a dedicated *ex-situ* treatment facility has been developed for these studies. This new facility was designed after our existing *ex-situ* treatment system⁷ but has its own separate reaction cell, welded feed line for sulfur-containing gases, and outlet discharge to an aqueous-based potassium hydroxide scrubber solution (Figure 1). The non-pristine system is, however, designed such that it shares a high temperature furnace with our pristine facility.

Small, supported copper particles were prepared on a standard, 200 mesh, holey-carbon-coated Mo TEM grid. The grid was initially given a 1 h *ex-situ* reduction at 600 °C in flowing (20 sccm) hydrogen in our pristine treatment facility. Various areas showing discrete, fully dense copper particles were imaged (Figure 2a), and particle locations were mapped out for re-examination. The grid was then placed into the non-pristine reactor and given a 0.25 h sulfidation treatment at 100 °C under a 10% H₂S/90% H₂ gas mixture. Metal particles previously analyzed were re-examined (Figure 2b). The development of a torus structure, similar to that observed during copper oxidation⁸⁻⁹ (Figure 3) and commonly associated with corrosion phenomena,¹⁰⁻¹¹ was observed. This work suggests that in the case of small copper particles, gas sulfiding may occur by the same general mechanism as oxidation.

REFERENCES

1. E.P. Butler and K.F. Hale **Dynamic Experiments in the Electron Microscope** (1981) Elsevier/North Holland Biomedical Press.
2. P.L. Gai, *Microscopy & Microanalysis* **3** (1997) 617.
3. E.D. Boyes, *Microscopy & Microanalysis* **3** (1997) 589.
4. P.A. Crozier, *Microscopy & Microanalysis* **7** (2001) 1058.
5. I. Chan, *J. Electron Microscopy Tech.* (1985) 525.
6. L.F. Allard et. al., *Proc. Microscopy & Microanalysis* **3** (1997) 595.
7. C.E. Kliewer et. al., *Proc. Microscopy & Microanalysis* **1** (1999) 926.
8. P. Gai et. al., *Nature* **348** (1990) 430.
9. C.E. Kliewer et. al., *Proc. Microscopy & Microanalysis* **6** (2000) 378.
10. M.G. Fontana and N.D. Greene **Corrosion Engineering** (1978) McGraw-Hill Inc.
11. P.G. Shewmon *Transformations in Metals* (1969) McGraw-Hill Inc.

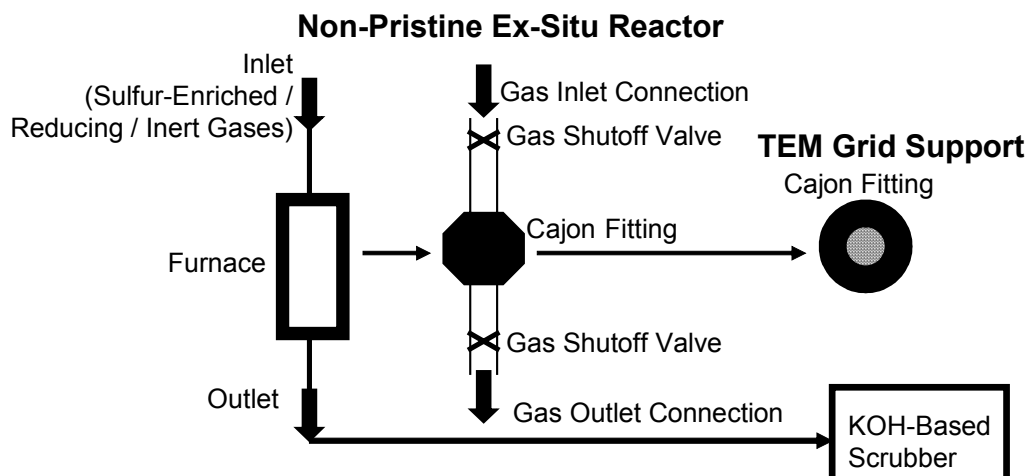


Figure 1: Schematic of *ex-situ* gas reactor system designed to treat materials in sulfur-rich environments. Reaction cell (center) is located within the furnace. Cajon fitting supports the TEM sample.

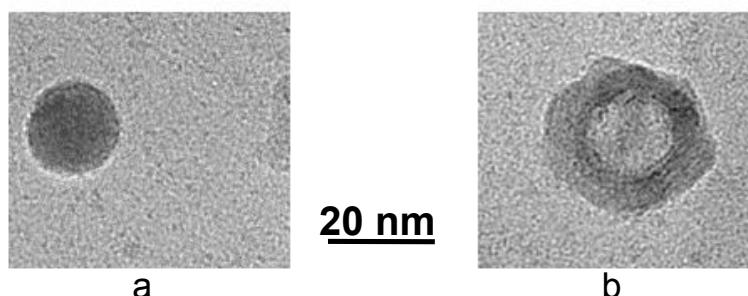


Figure 2: Bright field TEM images showing the general morphology of small, carbon supported copper particles (a) given a 600 °C/1 h *ex-situ* reduction treatment in hydrogen and then (b) given a subsequent 100 °C/0.25 h *ex-situ* sulfidation treatment in a 10% H₂S/90% H₂ mix.

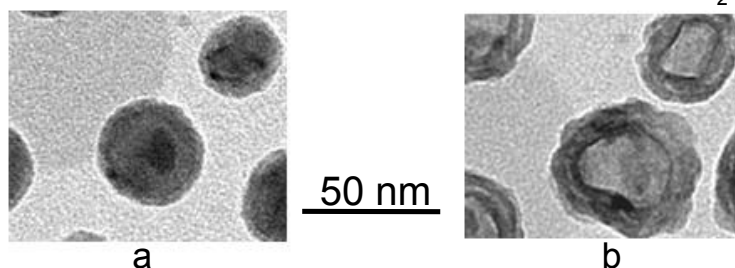


Figure 3: Bright field TEM images showing the general morphology of small, carbon supported copper particles (a) given a 600 °C/1 h *ex-situ* reduction treatment in hydrogen and then (b) given a subsequent 200 °C/2 h *ex-situ* air oxidation treatment.