

## ***In situ* EC-TEM Studies of Metal Thin Film Corrosion in Liquid Solutions at Elevated Temperatures**

Jeung Hun Park<sup>1,2</sup>, Tommy Watanabe<sup>3</sup>, Ainsley Pinkowitz<sup>4</sup>, David J. Duquette<sup>4</sup>, Robert Hull<sup>4</sup>, Daniel A. Steingart<sup>2</sup>, and Frances M. Ross<sup>1</sup>

<sup>1</sup>. IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, United States.

<sup>2</sup>. Department of Mechanical and Aerospace Engineering, and Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey 08544, United States.

<sup>3</sup>. Hitachi Metals America, Purchase, New York 10577, United States.

<sup>4</sup>. Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, United States.

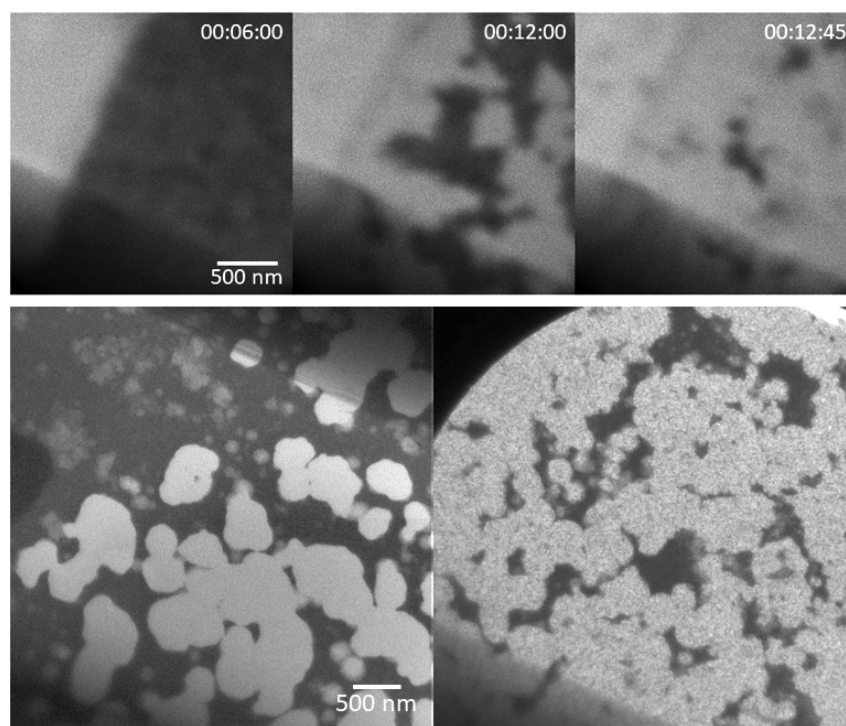
Different modes of corrosion are possible for metal films in contact with liquid solutions, depending on the metal or alloy present, the composition of the solution and conditions such as temperature and mechanical stress [1]. The difficulty of monitoring corrosion processes with good spatial and temporal resolution under a liquid layer creates a challenge for understanding key aspects of these corrosion processes, such as the nucleation sites and growth rates of individual pits during localized corrosion. However, structural changes and chemical processes at the solid/liquid interface can be probed by means of liquid cell transmission electron microscopy under electrochemical control (EC-TEM) [2]. This technique can provide a combination of electrochemical and temporally and spatially resolved data that has already yielded information on corrosion kinetics in liquid solutions [3]. Here, we use EC-TEM to examine galvanic dissolution processes of metal thin films, such as Cu and Ni, by exposure to ppm levels of chemical additives, typically Pd ions, in acidic solutions. We have examined the kinetics of these processes under conditions of different pH and Pd ion concentration, and will also discuss temperature-dependent corrosion reactions in these materials systems.

The experiments were carried out in a JEOL 2010F TEM operated at 200 kV using a continuous flow LC-TEM holder (Hummingbird Scientific Co., Ltd) with capabilities for mixing or exchanging solutions, as well as heating and electrochemical control. Metal films were deposited to thicknesses of 20-100 nm by electron beam evaporation. The films were deposited either over blank window chips or over commercially available heater chips that included an electrically isolated resistance heater built into the window. Patterning using either lithography or a stencil mask ensured that the metal film partially covered the liquid cell window to provide an open reference area for imaging during dissolution. After assembling the liquid cell, deionized water was introduced to remove air bubbles inside the cell. The metal film was imaged in water, then either deionized water continued to flow or a solution containing an acid electrolyte (H<sub>2</sub>SO<sub>4</sub>) and/or ppm levels of chemical additives (for example, PdSO<sub>4</sub>) was introduced. The film morphology was then imaged at regular intervals. The resulting structural changes were followed as a function of both the solution chemistry and the illumination conditions. The electron beam is well known to cause radiolysis of water that changes the solution chemistry, for example typically lowering the pH [4]. Unsurprisingly, both the solution pH and the beam intensity affect the rate and morphology of dissolution [5]. Figure 1 shows examples of galvanic dissolution of Cu in 0.1M H<sub>2</sub>SO<sub>4</sub> + ppm level of PdSO<sub>4</sub> and dissolution of Ni at lower electron beam flux. Experiments such as these provide information on the spatial distribution of the corrosion process (for example, distinguishing grain boundary pitting from intragranular pitting, and measuring locations of

deposited Pd), and the overall rate of the reaction as a function of solution composition. It is also possible to follow the process as a function of temperature, correlating the film morphology with the results of heating via current flow through the resistance heater built in to the liquid cell window. We will discuss how such experiments can provide insights into corrosion processes that may be useful in materials design.

#### References:

- [1] H.-H. Strehblow *et al.* in *Corrosion Mechanisms in Theory and Practice*, Third Edition, 2012, ed. P. Marcus (CRC Press, New York).
- [2] F. M. Ross, *Science* **350** (2015) aaa9886.
- [3] S. W. Chee *et al.*, *Chemical Communications* **51** (2015) 168.
- [4] J. H. Park *et al.*, *Nano Letters* **15** (2015) 5314.
- [5] J. H. Park *et al.*, *Science Advances* **3** (2017) e1700234.
- [6] We acknowledge financial support from the BP Carbon Mitigation Initiative and from NSF-GOALI (CMMI 1129722, DMR-1310639 and DMR-1309509). We also acknowledge the invaluable technical support of Dr Mark C. Reuter and Mr. Arthur W. Ellis of IBM.



**Figure 1.** (Upper row) Three images recorded during galvanic dissolution of a polycrystalline Cu film (dark region on right side of first image) in 0.1 M H<sub>2</sub>SO<sub>4</sub> + 50 ppm PdSO<sub>4</sub> flowing at 3 μl/min at room temperature. Dissolution begins at numerous sites. The time is shown in *hh:mm:ss* after the switch from deionized water to the acidic solution. (Lower row) Two images recorded during galvanic dissolution of a Ni film in 0.1 M H<sub>2</sub>SO<sub>4</sub> + 50 ppm PdSO<sub>4</sub> flowing at 3 μl/min. In the left image the film has already started to corrode at multiple locations.