

In-situ Electron Microscopy Observation of Initiation and Propagation of Wet H₂S Corrosion on Steel

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The in-situ nm-scale electron microscopy (EM) characterization of corrosion phenomena is a key point to understanding the mechanisms of initiation and propagation of failures. To conduct wet corrosion studies on metal surfaces, direct contact of the metal surface with water is required. So, to do in-situ EM experiments, a small nano-reactor is needed to keep the reaction environment separated from the high vacuum in the column of microscope. Liquid phase electron microscopy (LPEM) has been developed recently but the main limitations of this technique are beam damage and the thickness of the liquid in the electron beam direction [1].

In this research we present an approach to locally condense water on a thin TEM sample followed by in-situ STEM imaging to record the initiation of wet corrosion damages on steel. To this end, a nanoreactor (NR) consisting of a MEMS-based thermoelectric cooler (TECs) was fabricated. The NR is made of bottom and top chips of which the bottom chip is equipped with a planar TEC device. An oval ring seals the top part of this NR from the TEC MEMS device. A homemade TEM gas holder with inlet and outlet for purging the wet H₂S gas into the NR is designed and fabricated to hold the NR in the TEM column. (See **Figs. 1a-c**). A planar Peltier cooler on a thin SiN membrane (with thickness of 400-1 μm) is fabricated to dissipate heat from the central part of the membrane to the Si body of the MEMS device, enabling local water condensation by reducing T~10°C only on the sample area [2]. To allow usage of the chip in a corrosive environment the whole chip is covered with a 40 nm Al₂O₃ layer using atomic layer deposition (ALD). Later on, this layer is used as a hard mask to create an e-transparent carbon window on the SiN membrane. This TEC MEMS-based chip is schematically presented in **Fig. 1(d-e)**.

For fabrication of electron transparent windows, the backside of the TEC MEMS-based device was coated with 15nm of amorphous carbon layer using a e-PVD method. To open up the 5-7 μm circular window on the Al₂O₃ layer, the Ga beam in a FIB-SEM tool is used. The remaining SiN is removed using dry reactive ion etching method. The in-situ STEM image series was recorded during in-situ experiments using a FEI Monochromated Tecnai G2 operating at 200 keV (see **Fig.2**). The post-mortem EDS analyses were done using a TFS Talos equipped with Bruker superX detectors at 200keV accelerating voltage. As conclusion,

the locally condensed water on the membrane can be successfully applied to elucidate the mechanisms of pit initiation, corrosion product and passive layer formation. This technique shows high ability to real-time observation of the onset and growth of corrosion damages in nm-scale, thus far lacking [3].

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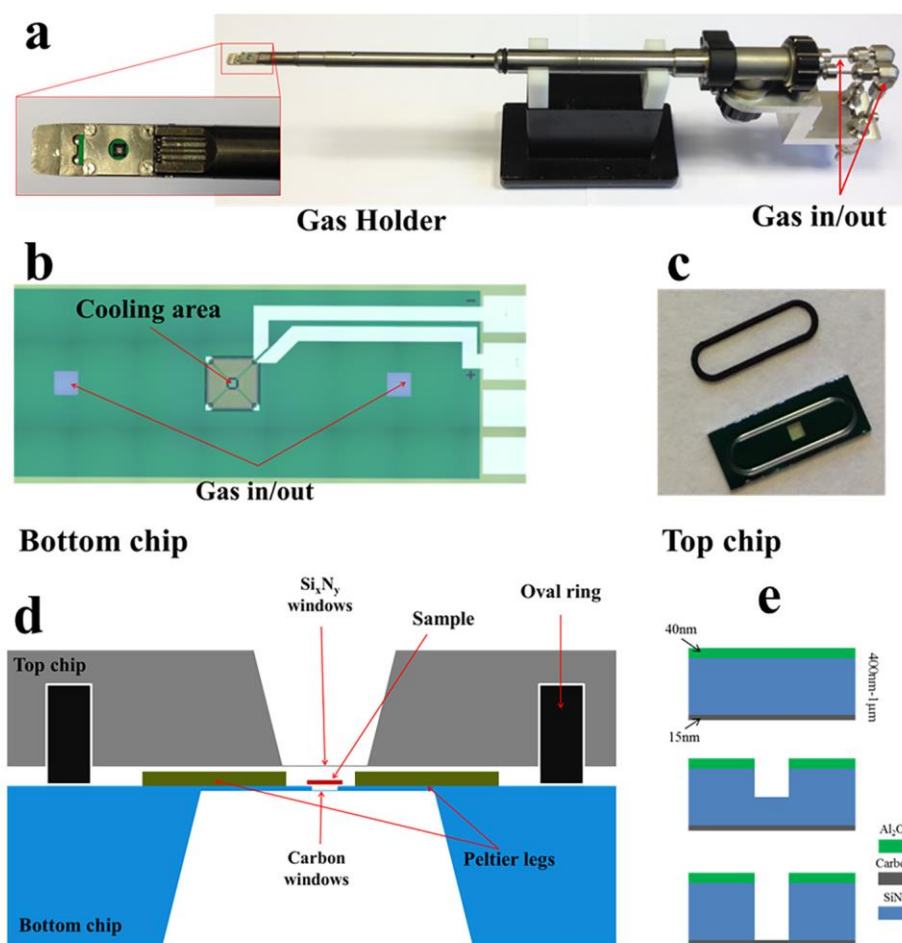


Figure 1. (a) a TEM gas holder with inlet and outlet to purge wet H_2S gas into the NR. (b) a MEMS based chip device equipped with a planar thermoelectric cooler to locally cool down the sample area. (c) top chip and oval-ring for sealing the NR and separating the sample area from high vacuum in TEM column. The top chip is made with a uniform SiN membrane with a thickness of 30nm. The membrane area was made in a square shape with dimensions of $30\mu\text{m}$. (d) the schematic of assembled NR loaded with sample (side view). (e) steps to produce thin e- transparent window on the SiN membrane.

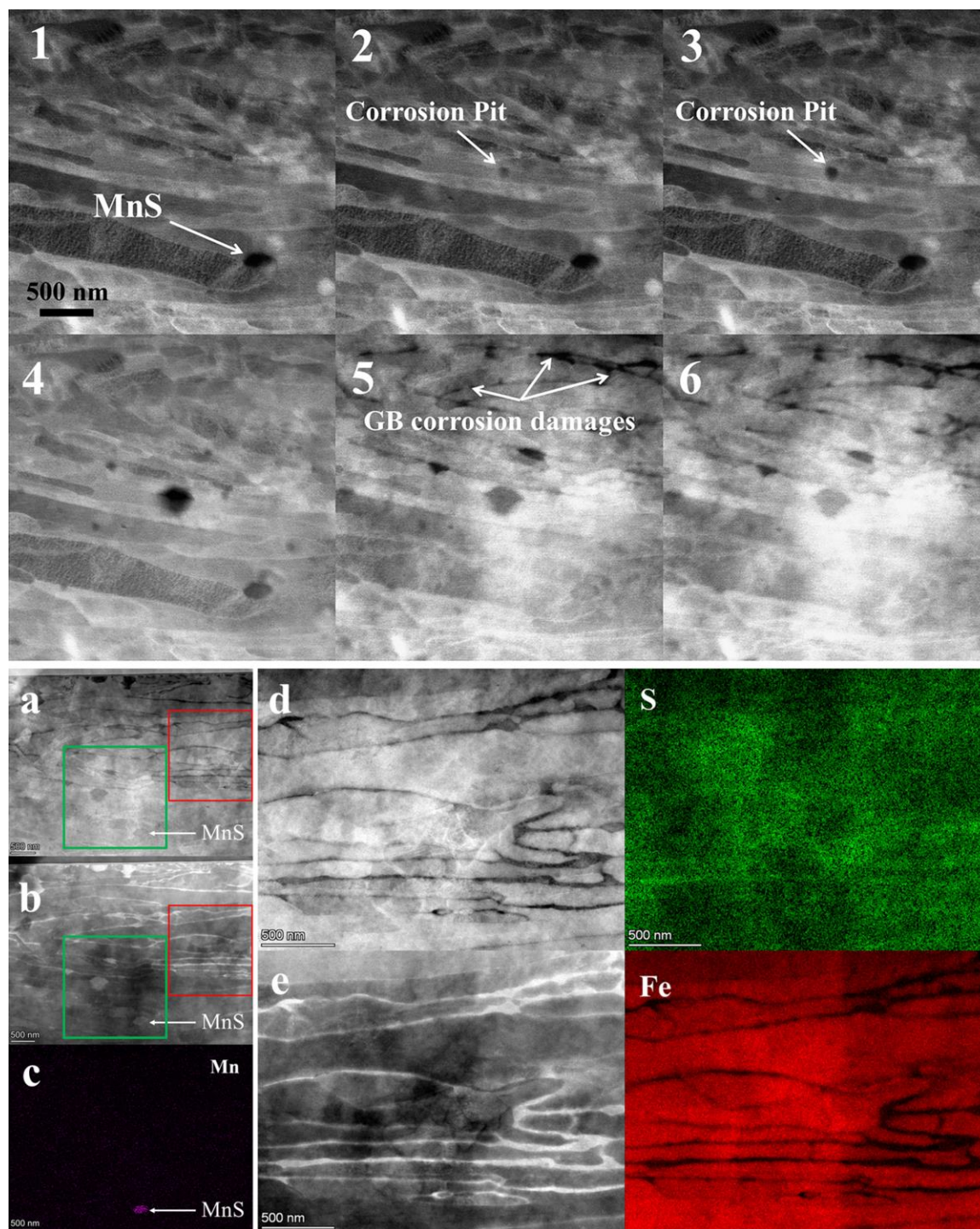


Figure 2. HAADF STEM image series recorded (1) before turning the Peltier device on and (2-6) the Peltier device is on. The time interval is 10 sec. MnS inclusion is shown in (1). Wet H₂S corrosion damages in the grain boundaries (GBs) are observed. Initiation and propagation of a corrosion pit in images (2-6) in the middle of pictures are imaged at each interval. At the beginning, by depletion of Fe ions, the intensity in the pit area drops and later on by forming the corrosion products, slightly greyish contrast appears in (5-6). In images (5-6) the white contrast appears which is due to formation and deposition of corrosion products (here iron sulfide) on the surface of the sample. (a-e) HAADF STEM images recorded from a corroded sample after in-situ EM corrosion studies. (a) HAADF and (b) DF STEM images. (c) STEM

EDS map extracted by collecting X-rays for Mn. (d) HAADF and (e) DF STEM images from red square shown in (a-b images). Colored images show corresponding STEM EDS maps of S and Fe from "d-e". The green square in "a-b" represents the area from which in-situ image series were recorded (shown in image series 1-6).

References

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