

## In-Situ Observation and Formation Mechanism of Iron Surface Oxidation in the Initial Stages at 1,150 °C

Ming Zhong<sup>1</sup>, Yining He<sup>1</sup>, Elyce Milligan<sup>1</sup>, Chris Pistorius<sup>1</sup>, Bryan Webler<sup>1</sup>

<sup>1</sup>Carnegie Mellon University  
5000 Forbes Ave, Wean Hall 4317, Pittsburgh, PA, USA 15213  
Phone: (412) 268-3675  
Email: webler@cmu.edu

Keywords: *In-situ* observation, Surface oxidation, High temperature, Pure iron

### INTRODUCTION

Steel is an irreplaceable material in the modern world, and the world crude steel production in 2017 was 1691.2 Mt. [1] Because the steel is exposed to air at high temperatures during conventional hot-rolling processes, iron oxide scales are inevitably formed. There are three kinds of oxide scales: primary scale, secondary scale, and tertiary scale depending on the formation location. [2–13] Scale formation can lead to uneven roll wear and strip shape defects, and it is also a source of surface defects. [14, 15] During cooling after coiling the oxide scale can grow and also undergo structural changes. [7, 15] Any iron oxidation represents yield loss and the surface scales can sometimes affect the downstream cold rolling and the pickling process. [2]

There have been many studies characterizing the evolution of oxide scales on iron and steels. [2–32] Iron forms a three-layer scale during oxidation in air, with the innermost layer wüstite ( $\text{Fe}_{(1-\delta)}\text{O}$ ) in contact with metallic iron, then magnetite ( $\text{Fe}_3\text{O}_4$ ), and hematite ( $\text{Fe}_2\text{O}_3$ ) in contact with the gas. [7, 16, 33–43] The rate of iron oxidation is controlled by diffusion of iron ions through the wüstite layer. At short times and thin scales, gas phase mass transfer has been suggested to control the oxidation rate. [3, 33–35] Many fundamental studies have focused on the thermodynamics, diffusion in wüstite, magnetite, and hematite, and the relative thicknesses of the oxide layers. [2–43]

Scale microstructure and layer thickness greatly influences the effectiveness of pickling. [44–46] Meanwhile descalability of scale is strongly dependent on its microstructure, which further influences the surface quality. [47–50] Clarifying scale microstructure formation is imperative, particularly the evolution process during oxidation. Previous studies have attempted this by applying the hot-stage environmental scanning electron microscopy (HSE-SEM) to observe the initial stage of iron surface oxidation. [51–54] During oxidation, both cavity (pit) and pyramidal shape on the surface were observed. Also, the formation of iron-oxide whiskers was confirmed during cooling. However, the oxygen partial pressure was restricted to a low value which does not reflect industrial conditions.

More relevant conditions can be achieved in the confocal scanning laser microscope with a hot stage (CSLM). There was one particularly relevant study used CSLM to study surface oxide morphology changes during initial oxidation with dry air. [13] At the beginning, a faceted surface appeared and grain grew with the oxidation. Then the whole surface was replaced by tiny and irregular crystals as a third oxide phase (front reaction) sweeps over the surface during around 20–30 seconds oxidation. Meanwhile, the internal oxide layers were reported as the previous studies, but without a clear hematite layer. The authors proposed a hypothesis to explained the morphology change which differed from previous HESEM work. [13, 51–53] In addition, only a 30 seconds oxidation experiment was done, so additional time points could help clarify the oxide surface evolution.

In this work, iron samples were oxidized in air from 2 seconds to 60 seconds. *In-situ* CSLM results were compared with the *ex-situ* SEM tests. Two reaction fronts appeared to move across the field of view which was confirmed happened from the edge to the center part was observed with increasing the surface roughness considerably. The cross-section of samples was confirmed by an optical microscope with a polarized light source. Different oxide layers within the scale were identified clearly, and the over-oxidation at the sample edge was confirmed. Moreover, the cross-section of samples was also confirmed by SEM, and the thicknesses of the oxide layer were summarized which increased parabolically with time.