

STEM Characterization of Metal Dusting Corrosion in Ni-based Alloy 600 and Fe-based Alloy 800H Exposed to a High Pressure Environment

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Metal dusting corrosion is a severe failure mechanism in metallic materials in the petrochemical industry. This form of degradation typically occurs when alloys expose to reducing gaseous environments (CO, H₂, CO₂, H₂O, and CH₄) with and high carbon activity ($a_c > 1$) at a median temperature range (400 – 800°C). Formation of graphite, carbides, and metal dusts on alloys significantly damage the working components. The early establishment of continuous Al₂O₃ scales on the alloy surface can limit graphite nucleation or/and impede inward diffusion of carbon [1,2]. Coupled with this are several recent studies which have shown that susceptibility to metal dusting tends to be much greater under high-pressure exposure conditions [3,4]. Despite the practical importance, studies of metal dusting mechanisms and strategies for improving dusting resistance under pressurized environments are still very limited.

The present work aims to study and compare the microstructures, chemical compositions, and crystallography of oxide scales formed on selected alloys during exposure to controlled dusting conditions at 1 bar and 18 bar. Specifically, we conducted integrated electron beam characterizations on the Ni-based alloy 600 (Ni-17Cr-8Fe) and Fe-based alloy 800H (Fe-31Ni-20Cr) exposed for 250 h at 620°C to 18 bar or 1 bar gas mixtures containing H₂, CO, CO₂, H₂O, and CH₄. The carbon activities at 18 bar and 1 bar were calculated to be 163 and 9, respectively. Pitting was observed on alloy 600 tested at 18 bar (Fig. 1 (a)), while only a limited number of pits were found on the sample exposed at 1 bar (Fig. 1 (b)). Carburization zones comprised of an outer zone of Cr₃C₂ lamellae in an austenitic metal matrix and an internal zone containing the lower chromium carbide, Cr₂₃C₆, were observed beneath pits in the 18 bar sample. STEM images (Fig. 3 (a)) and corresponding EDS analysis indicated that the 50 – 150 nm oxide scales consisted of an outer Cr₂O₃ layer and an inner SiO₂+Al₂O₃ layer. Such protective scales were found on the non-attacked surfaces of both samples. Interestingly, ~ 1 nm wide graphite plates were commonly found at Cr₂O₃ grain boundaries near the gas/scale interface in the sample tested at 18 bar (Fig. 3 (b)). No graphite plates were found in the Cr₂O₃ scale formed at 1 bar. The formation of these graphite plates may provide fast paths for inward carbon diffusion and, hence, lead to the onset of metal dusting during exposure to the pressurized environment. This novel observation of graphite plates formed within a thermally grown Cr₂O₃ scale is inferred to be an important aspect of the dusting mechanism at high pressures and will be a topic of further investigation.

Metal dusting corrosion was much more severe on the 800H alloy tested at 18 bar than at 1 bar. Formation of graphite, cementite, iron/chromium oxides, and metal dusts were found in the pitted areas of the 18 bar exposed sample. STEM images (Fig. 4 (a) and (b)) and the corresponding EDS analysis indicated that formation of a continuous Cr₂O₃ scale is the main – albeit finite – protective mechanism for both samples. Consistent with the 600 alloy, graphite plates were only found in the 18 bar sample. Further, a relatively high Fe content (up to 3.2 at%) was found in the Cr₂O₃ scale formed at the 18 bar sample, suggesting that the presence of Fe in the scale may play a role in facilitating graphite nucleation.

References:

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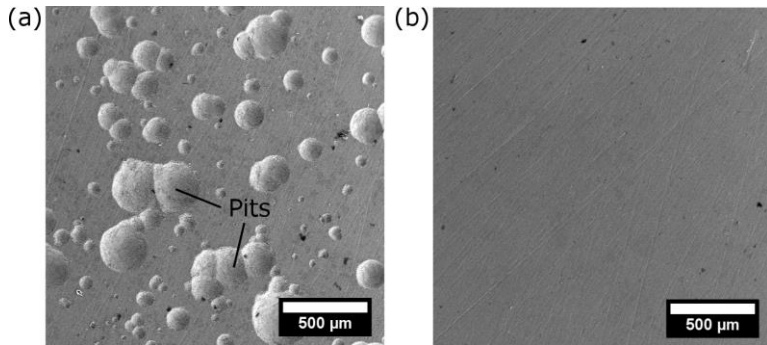


Figure 1. SEM images of the surfaces of the alloy 600 tested at (a) 18 bar and (b) 1 bar at 620°C for 250h

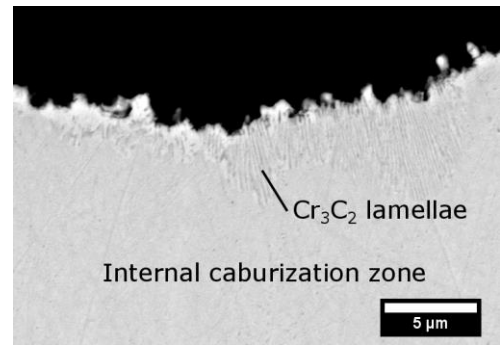


Figure 2. SEM BSE cross-sectional image of pit area in the alloy 600 tested at 18 bar and 620°C for 250h

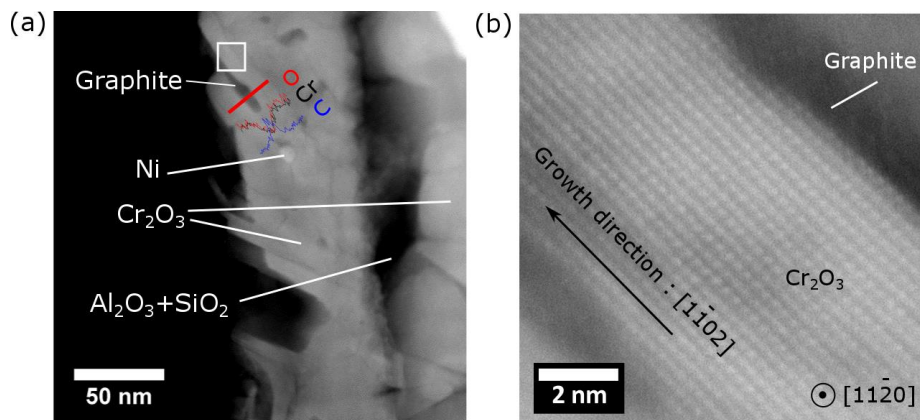


Figure 3. STEM HAADF images of (a) scale on alloy 600 tested at 18 bar with EDS (red line), showing graphite at the Cr₂O₃ boundary, and (b) white box area in (a), showing Cr₂O₃/graphite interface

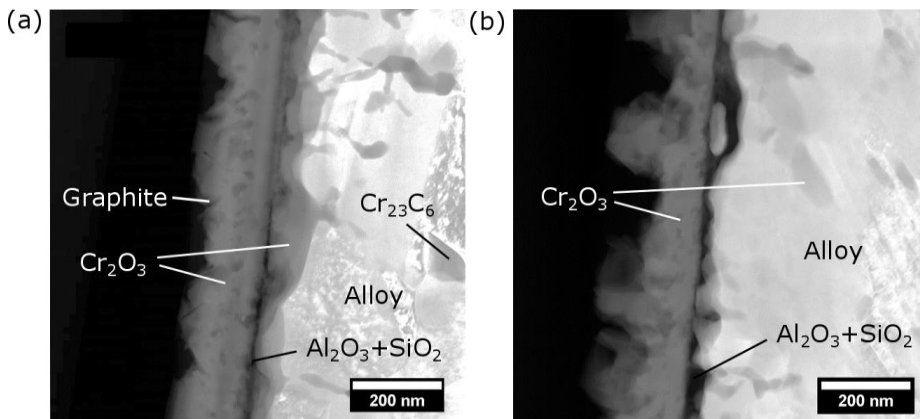


Figure 4. STEM HAADF images of the scales on the alloy 800H tested at (a) 18 and (b) 1 bar at 620°C for 250h