

On the origin and state of Ni and Fe species as catalysts for the initiation of metal dusting corrosion

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1 Introduction

Metal dusting corrosion constitutes a serious issue in a range of chemical industries [1–3], where a mixture of CO, CO₂, H₂, steam and hydrocarbons meets metals and alloys at elevated temperatures ($T > 400$ °C) under low oxygen/steam partial pressures (P_{O_2}/P_{Steam}). The first stages of carbon formation that initiate metal dusting are analogous to carbon formation issues on the heterogeneous catalysts applied in the petrochemical industry. The thermodynamic driving force is hence given by the activity for carbon formation (a_C), and metal dusting is prevailing under $a_C > 1$. The formation of solid carbon is nevertheless strongly controlled by kinetics; it rarely forms in the gas phase, even at very high a_C . Ni and Fe are excellent catalysts for carbon formation. Unfortunately, they are also the main constituent elements of common industrial alloys. Hence their stability in alloy matrix is critical for metal dusting.

The overall objective of this study is to advance the understanding of the initiation of metal dusting corrosion. In our recent work, improved understanding of the initial carbon formation and the role of the protective surface oxide layer was obtained through a comprehensive experimental investigation, together with advanced surface and bulk characterization. We have established that the surface oxide layer composition, thickness and structure as affected by pretreatment temperature, oxidant partial pressure and sample preparation procedure strongly affects the susceptibility to form solid carbon [4–6]. Here we further proceed to study the nature and localization of Ni/Fe phases at the surface within and/or below the surface oxide layer formed as a result of the pre-oxidation and how they are accessed by the reducing atmosphere during syngas exposure.

2 Experimental

A set of coupon-like alloy (INCONEL® 601) samples were subjected to oxidation at different temperatures for 6 h under 10% steam/inert (at 1 bar). Then some of the pretreated samples were exposed to carburizing syngas mixtures with either *infinite* (10%CO in Ar, 1 bar) or *finite* (20% or 50% CO in H₂/CO₂/steam/Ar, 20 bar) carbon activity ($a_C \gg 1$ or $a_C > 1$). The duration of the syngas exposure was also varied.

The resulting surfaces and carbonaceous products were characterized by means of optical imaging and light-optical microscopy, scanning electron microscopy (SEM), depth profile analysis by Auger electron spectroscopy under ion-sputtering, transmission electron microscopy (TEM) equipped with energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS).

3 Results and discussion

Pre-oxidation at 540 °C provided samples covered by a Cr and Al rich, thin oxide layer. SEM reveals carbon formations on all such samples subjected to CO exposure at *infinite* a_C , increasing with exposure time as expected. The amount of carbon formed during 1 h CO exposure treatment cannot be detected by visual inspection, but thin carbon filaments could be observed in high magnification covering part of the initial surface. The formation of filaments and complementary TEM/EDS results point to the presence of metal nanoparticles containing Ni and/or Fe, and such short exposures represent a basis for an accelerated experimental protocol to reveal the origin of these particles within the surface oxide layer. Higher pre-treatment temperature under oxidizing conditions lowers the susceptibility to carbon formation, and the critical factors to and durability of this effect will be further discussed and investigated.

Under *finite* a_C conditions, thick carbon deposits were obtained at 650 °C and 750 °C while no (20%CO) or little (50%CO) carbon was found after syngas exposure at 550 °C. Hence, under different CO concentration but constant level of H₂, CO₂ and steam, the amount of carbon formed is clearly a function of exposure temperature and gas composition. The former clearly demonstrates the kinetic control of the (exothermic) reactions. Removal of carbonaceous deposits revealed that material degradation had taken place at higher temperatures (either ‘pitting’ or ‘spallation’). As shown by Auger depth profile analysis, oxidation of the alloy matrix had proceeded alongside the reducing reactions leading to carbon formation under exposure to the 20%CO containing gas mixture at higher temperatures, while this was not the case under 50%CO. The TEM and EDS results show that the formation of filamentous carbon deposits under *finite* a_C conditions also was catalyzed by metallic particles containing Ni and Fe.

XPS is currently being used to examine the oxidation states of the different species that exist in the near surface region. A next step will be detailed TEM/EDS analysis of the near surface region by a combination of carefully prepared cross-sections and micro/nano-scale samples obtained via Focused Ion Beam (FIB).

4 Conclusions

We have established protocols to investigate the catalytic properties of high temperature alloy surfaces, and factors leading to (*unwanted*) carbon formation and subsequent metal dusting, under both simplified ($a_C \gg 1$, low pressure) and more industrially relevant (syngas, $a_C > 1$, high pressure) conditions. The experiments verify the kinetic nature of these phenomena and point to the importance of the structure and composition of the protective surface oxide layer as resulting from the conditions of the preceding oxidative treatment. The metal dusting hence appears to be strongly linked to the inclusion of Ni/Fe species in the oxide surface layer, which subsequently reduce to facilitate carbon formation.

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