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Investigating the metal dusting behaviour of surface modified 304L stainless steel

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Abstract

Metal dusting is a catastrophic carburisation process where the affected metal is weakened by embrittlement due to an increase in carbon content and it subsequently disintegrates. The high velocity gases found in metal dusting environments erode away the brittle material resulting in the metal dusting corrosion product – coke, metal oxides and graphitic carbon. Environments favourable for metal dusting contain high carbon activities ($aC > 1$) at temperatures of 400-800^{o}C and oxygen partial pressures as low as 10^{-24} atm. Such environments are encountered in the chemical, petroleum and petrochemical industries where syngas (H_2-CO-H_2O-CO_2) and hydrocarbons are converted into other useful products.

The objective of this work was to design an experimental rig that simulates a metal dusting environment and then study the behaviour of two types of surface modifications on 304L stainless steel exposed to a metal dusting environment. The two surface modification methods were: (a) copper electroplating using the pulse plating method at varied deposition times of 30, 45 and 60 minutes and (b) laser cladding 304L with ruthenium of varied concentrations in the range (0-5 wt.%Ru).

The following conditions were used to simulate the metal dusting environment; a gas mixture of 20 vol.% CO- 60 vol.% H_2- 20 vol.% H_2O, at 525^{o}C and 650^{o}C, with resultant carbon activities of 0.679 and 0.512 atm respectively. And oxygen partial pressures of 1.599×10^{-27} at 525^{o}C and 5.118×10^{-24} atm at 650^{o}C. An additional metal dusting environment with a relatively high carbon activity was simulated. This environment contained a gas mixture of 25 vol.% CO- 75 vol.% H_2, at 650^{o}C with a carbon activity of 35 atm and an oxygen partial pressure of 1.012×10^{-24} atm. The samples were exposed for a total of 21 days and analysed after seven days and after 21 days of exposure. The samples were analysed using FESEM, Raman Spectroscopy and GIXRD.

The results showed that the copper plated samples performed the best in terms of protecting the 304L stainless steel against metal dusting. However, the copper coating was susceptible to oxidation which could not be slowed down. Increasing

deposition time resulted in increased coating thickness which in turn resulted in prolonged protection against metal dusting by the copper coating. However, a longer exposure time would result in the eventual removal of the copper by oxidation, exposing the 304L stainless steel substrate as was the result in the sample exposed at 650^{o}C, in the gaseous environment with a carbon activity of 35 atm.

The ruthenium laser cladded samples performed well in the low carbon activity environment particularly at 525^{o}C. Metal dusting initiation began 21 days on only the 2 wt.% Ru sample. Exposure at 650^{o}C resulted in the spalling of the oxide layer formed on the samples and the initiation of metal dusting within seven days of exposure. However, in the low carbon activity environment the samples were able to self-heal and maintain relatively low levels of attack. Only pits smaller than 1 μm had formed on the substrate that was exposed as a result of the spalling of the oxide.

Samples exposed to the high carbon activity (35 atm) environment revealed that the high ruthenium (2-5 wt.%) containing samples were highly susceptible to metal dusting, resulting in large pits greater than 20 μm. The pitting occurred at the areas enriched with ruthenium. In contrast, the low ruthenium content samples (0 and 0.5 wt.% Ru), underwent metal dusting initiation as opposed to pitting even after 21 days of exposure. It was identified that to achieve maximum benefit from the ruthenium laser cladded samples against metal dusting, a single phase coating may be applied.