

The Breakdown of the Protective Oxide on 11% Chromium Steel
The Influence of Water Vapor and Gaseous KCl

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ABSTRACT

The first part of this thesis is focused on the influence of water vapour on the oxidation of X20 steel (CrMoV 11 1). Three parameters were investigated; $p_{\text{H}_2\text{O}}$, gas velocity and temperature. The oxidation process was observed by gravimetry and by a number of surface analytical methods, the most important being ESEM/EDX, GI-XRD and GDOES. In dry O_2 at 600°C the material forms a protective chromium-rich $\alpha\text{-(Cr,Fe)}_2\text{O}_3$ oxide. In mixtures of oxygen and H_2O , chromium is lost by vaporization, in the form of $\text{CrO}_2(\text{OH})_2(\text{g})$. Chromium loss depletes the oxide in chromium. The rate of chromium evaporation and the rate of supply of chromium to the oxide determine whether the alloy will form a protective oxide or not. At low evaporation rates the supply of chromium to the oxide by diffusion from the steel substrate is sufficiently rapid so that the protective properties of the oxide are not destroyed. With increasing evaporation rate, the supply of chromium to the oxide eventually becomes insufficient to compensate for chromium vaporization, with the result that chromium depletion also affects the oxide at the oxide/metal interface. When all of the oxide has become chromium-poor and non-protective, the oxidation rate increases dramatically. As a result, a thick layered scale is formed consisting of an inner FeCr-spinel layer and outer hematite layer.

The loss of chromium and the tendency to destabilize the protective oxide increases with the concentration of water vapour. For example, the material suffers breakaway corrosion after 336 hours in $\text{O}_2+40\%\text{H}_2\text{O}$ while the rate of oxidation is only marginally increased in the presence of $10\%\text{H}_2\text{O}$. The tendency towards chromium depletion and breakaway corrosion in $\text{H}_2\text{O}/\text{O}_2$ environment increases with gas velocity. This is because the transport of gaseous species away from the surface becomes more rapid as the flow rate increases. Below a certain gas velocity chromium vaporization does not accelerate oxidation in $\text{O}_2+40\%\text{H}_2\text{O}$. Increasing gas velocity above a critical level triggers a huge mass gain (two orders of magnitude larger than in dry O_2).

Increasing the temperature affects the oxidation of stainless steel by increasing chromium evaporation from the oxide, and by increasing chromium diffusion in the metal and in the oxide. The increased chromium loss and the increased diffusion through the oxide tend to increase the rate of oxidation as temperature increases. In contrast, the higher rate of diffusion in the alloy increases the supply of chromium to the oxide/metal interface, increasing the chromium content of the oxide and making the oxide less vulnerable to chromium loss by vaporization. The temperature dependence of oxidation is expected to depend on the combination of these effects. In some cases, the interplay of these factors leads to an inverse dependence of oxidation rate on temperature, for example in $\text{O}_2+40\%\text{H}_2\text{O}$ in the range $500\text{--}550^\circ\text{C}$.

The second part of the thesis deals with the effect of gaseous KCl on oxidation. The initial stages of oxidation of X20 steel (CrMoV 11 1) stainless steel at 600°C are strongly accelerated by $\text{KCl}(\text{g})$ at temperatures above the dew point of the salt. In the absence of $\text{KCl}(\text{g})$, a protective chromium rich oxide ($(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_3$) forms. $\text{KCl}(\text{g})$ reacts with chromium in the oxide scale forming K_2CrO_4 leading to the formation of non protective hematite, Fe_2O_3 and resulting in a loss of the protective properties of the oxide. As a result the oxidation rate is accelerated. This finding may help explain the corrosion behaviour of stainless steels in environments with high levels of KCl, e.g., in fireside corrosion in biomass-fired power plants.

Keywords; Oxidation, breakaway corrosion, 11% Cr-steel, water vapour, flow rate, temperature dependence, chromium evaporation, $\text{CrO}_2(\text{OH})_2$, $\text{KCl}(\text{g})$