Abstract

This thesis deals with the oxidation of austenitic stainless steels in O_2/H_2O mixtures at 500-900°C. Due to their ability to form a protective chromium-rich $(Cr,Fe)_2O_3$ oxide, austenitic stainless steels are often used in high-temperature applications. In environments containing $O_2 + H_2O$, for example in biomass combustion, this group of alloys tends to suffer an acceleration of corrosion.

Four different austenitic stainless steels were exposed in a well-controlled environment in the laboratory. After exposure the oxidized samples were analyzed by a number of analytical techniques including GI-XRD, ESEM, TEM and SAM.

This thesis shows that the oxidation of stainless steel in oxygen is strongly influenced by the presence of water vapour. The results show that water vapour induced chromium evaporation is a key process causing the breakdown of protective oxide scales on austenitic stainless steel. In the presence of O_2+H_2O, chromium is vaporized in the form of $CrO_2(OH)_2$. Chromium evaporation causes a depletion of Cr in the protective oxide and in the steel substrate. If the evaporation rate is high enough, the Cr concentration in the oxide drops below a critical level. This causes the oxide to lose its protective properties and to become similar to the non-protective α-Fe_2O_3.

The rate of chromium evaporation depends on the water vapour concentration, gas velocity and temperature. The oxidation behaviour of the steels investigated is explained in terms of the supply of chromium from the substrate to the oxide. It is shown that the resistance of a steel towards high temperature corrosion in O_2/H_2O mixtures is enhanced by a high Cr/Fe ratio, by fast diffusion in the steel bulk (ferrite rather than austenite), and by a high density of steel grain boundaries (small grain size).

A qualitative mechanism is postulated describing the breakdown of the protective Cr-rich $(Cr,Fe)_2O_3$ scale in the presence of O_2/H_2O.

KEYWORDS: active corrosion, austenitic stainless steel, oxidation, chromium vaporization, water vapour, iron-chromium oxide, breakdown of protective properties