Resistance of Chromia Scales to Mixed Gas Corrosion

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Chromia-forming alloys are successfully used at moderately high temperatures to resist corrosion by dry air or oxygen. However, in many energy conversion processes other gaseous corrodents (CO_2, SO_2, H_2O, etc.) are encountered. In these atmospheres, the alloys experience accelerated failure, going into breakaway (rapid) corrosion, either locally or more generally. Examples include corrosion of heat-resistant steel by CO_2, causing simultaneous external oxidation and internal carburisation. Likewise, corrosion by SO_2 produces mixed oxide-sulfide scales on a variety of metals and alloys.

Corrosion in mixed gases gives rise to some surprising effects. Chromia scales grown in CO-CO_2-N_2 develop layers of both carbide and nitride beneath the oxide, but chromia grown in H_2-H_2O-N_2 is impermeable to nitrogen. Similarly, addition of SO_2 to CO-CO_2-N_2 suppresses Cr_2N formation, even when p_{SO_2} is too low to stabilize external sulphides.

Long ago, these results were interpreted as meaning that corrodent species shared the use of localized diffusion paths through the scale, and interacted with each other in those locations. This has now been verified by recent results which show that both carbon and sulphur are located on oxide grain boundaries in growing chromia scales. Hydrogen has also been found within chromia scales, but its location remains uncertain.

Possible chemical forms of grain boundary species are considered and mechanisms of their interaction are discussed with reference to the resulting scale transport properties.