Laser Raman microscopy study of the transition from high temperature alloy passivation to breakaway oxidation

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Model chromia-forming alloys were exposed to flowing gas mixtures of Ar-20CO_2, Ar-20CO_2-5H_2O and Ar-20CO_2-20H_2O (volume %) at 650^{o}C for periods of up to 336 h. The alloys were ferritic Fe-20Cr and Fe-25Cr (weight %), austeno-ferritic Fe-20,25Cr-10Ni and austenitic Fe-20,25Cr-20Ni. Initially, slow oxidation was observed for all alloys, but subsequent acceleration in the reaction rates led to unacceptably high rates of alloy consumption. In contrast, reaction in air led to stable, protective oxidation of these alloys.

Laser Raman microscopy was used to observe the evolution in oxide phase constitution accompanying the transition from protective to breakaway oxidation. In the protective stage of reaction, a passivating scale of Cr_2O_3 was formed by all alloys. Microanalysis by energy dispersive X-ray spectrometry of alloy subsurface regions allowed quantification of chromium depletion, and confirmation via a mass balance that the chromia scale contained negligible iron. Local fluctuations in chromia scale thickness (and the accompanying extent of alloy depletion) were observed to develop during the protective stage.

Acceleration in alloy reaction rates was due to nucleation and growth of additional iron-rich oxide nodules. Raman analysis showed that early in their lives, these nodules consisted of iron-rich M_2O_3 overlying a seemingly intact layer of chromium-rich M_2O_3 which was continuous with the protective scale surrounding the nodule. Beneath the chromia layer, internal precipitation of spinel, $Fe_{3-x}Cr_xO_4$, developed within the alloy. In the case of alloy Fe-20Cr, these nodules spread and coalesced to form a thick, continuous scale. This scale was found by Raman analysis to consist of a thin, outermost layer of Fe_2O_3 surmounting a thick Fe_3O_4 layer, a thin intermediate band of spinel ($x = 1.6$) and an inner two-phase layer of spinels with $x = 0.3$ and 1.2.

An Fe-25Cr alloy was more resistant to breakaway oxidation, forming some areas of thick, iron-rich oxide growths, but also some areas of "rehealed" oxide. The latter consisted of rather thin iron-rich M_2O_3 and M_3O_4 layers over a layer of chromium-rich oxide, either spinel or M_2O_3. Nickel-bearing alloys developed qualitatively similar scales. Nodule development on the 20Cr alloys was slower than on the ferritics, as a result of slow diffusing $NiFe_2O_4$ formation in the inner layer. At the 25 Cr level, both nickel bearing alloys formed nodules which were extremely slow growing, and too small for analysis.

The morphological evolution of fast growing, layered oxide scales from initially protective chromia is discussed in terms of alloy depletion leading to formation of spinel at sites of local damage to the chromia. This spinel permits outward iron diffusion and inward oxygen transport. Lateral diffusion then leads to nodule spreading both above and below the prior chromia layer, its consequent destabilisation and absorption into the scale.