High temperature oxidation of slurry coated interconnect alloys

In this project, high temperature oxidation experiments of slurry coated ferritic alloys in atmospheres similar to the atmosphere found at the cathode in an SOFC were conducted. From the observations possible interaction mechanisms between the slurry coatings and the growing oxide scale on the alloy surface were formulated. These mechanisms are a step towards deeper knowledge of how to design a coating/alloy combination with satisfactory performance in an SOFC-stack. A satisfactory performance entails a low growth rate of the forming oxide scale on the alloy surface and a low chromium content and resistance in this oxide scale.

Slurry coated ferritic alloy samples were oxidized long term in air containing 1% water at 900°C to measure the oxidation rate of the coated samples. The ferritic alloys included in the study were Crofer 22APU and Sandvik 1C44Mo20. Some complementary experiments were also performed on extra Sandvik alloys. The slurry coatings consisted of perovskite, spinel, corundum, and rutile oxides and they were both applied as single layer coatings and as dual layer coatings. Cross-sections of the oxidized samples were analyzed with scanning electron microscopy, SEM, and energy dispersive spectrometry, EDS. From these analyses information about the microstructures and the compositions of the grown oxide scales were collected. Based on the oxidation rate measurements for the single layer coated alloy samples three possible interaction mechanisms between the coating and the growing oxide scale were formulated:

A Surface covering coating
B Surface covering coatings with chemical reaction with the forming oxide
C Incorporation of coating particles

In the interaction mechanism A the coating particles are pushed ahead of the outwardly growing oxide scale. Coatings with this interaction mechanism mainly give a geometrical protection against oxidation by blocking oxygen access at the surface of the oxide scale. The protecting effect is gradually reduced as the oxide scale grows thicker than the diameter of the coating particles. Interaction mechanism B entails a chemical reaction between the growing oxide scale and the coating particles at the same time as these are pushed ahead of the growing oxide scale. The chemical reaction leads to a change in the oxide composition. In the third and last interaction mechanism, C, the coating particles are incorporated into the growing oxide scale. The incorporated coating particles create a geometrical protection against oxidation that should not loose their effect after the oxide scale has grown thicker than the diameter of the coating particles.

The two single layer coatings consisting of (La$_{0.85}$Sr$_{0.15}$)MnO$_3$ + 10% excess Mn, LSM, and (La$_{0.85}$Sr$_{0.15}$)CoO$_3$ + 10% Co$_3$O$_4$, LSC, coatings were found to be relatively successful in decreasing the oxidation rate, the chromium content in the outermost part of the dense scale, and the electrical resistance in the growing oxide scales when applied onto Crofer 22APU. But, the positive effects of the LSM and LSC coatings were significant enhanced when they were combined with an inner Co$_3$O$_4$ coating layer. However, for the Sandvik 1C44Mo20 samples the samples coated with Co$_3$O$_4$ + LSM only displayed a slight decrease in the oxidation rate compared to the LSM coated samples. For the Sandvik 1C44Mo20 samples coated with Co$_3$O$_4$ + LSC a drastic increase in the oxidation rate was observed compared to the Sandvik 1C44Mo20 samples coated with LSM. A significant amount of chromium in the oxide scale on the Co$_3$O$_4$ + LSC coated Sandvik 1C44Mo20 samples was furthermore detected. The cobalt rich coatings’ success on Crofer 22APU alloy samples and their failure on Sandvik 1C44Mo20 samples are believed to depend on the manganese access in the coating/alloy system. It appeared that a certain amount of manganese was acquired to stabilize the oxide growth on the alloy samples coated with cobalt rich coatings. This was supported by complementary oxidation of Co$_3$O$_4$ + LSC coated Sandvik alloys with varying manganese contents. Based on the microstructures of the formed oxide scales on all Co$_3$O$_4$ + LSC coated Fe-22Cr alloys samples included in this study and their observed weight gain, it was established that an optimal manganese content in the alloy on ca. 0.3-0.5 wt.% is a requirement to stabilize and utilize the positive effects of a cobalt rich coating.