Solid Oxide Fuel Cells (SOFCs) are currently the only fuel cells under development that can be operated in a wide temperature range, from 600 °C to 1 000 °C. Interconnects provide electrical connection between the cathode of one cell and the anode of the neighbouring one. At the same time they act as a barrier between the fuel, supplied at the anode, and the oxidant from the cathode. For low and intermediate temperature SOFC, ferritic stainless steels can be used as interconnects offering low materials costs and high workability when compared to ceramic interconnects. At the cathode side both O₂ and H₂O are present. If air is used as an oxidant, it has been observed that breakdown oxidation on the surface of the steel can occur after long annealing at high temperature. Also, Cr-based volatile species evaporate and reduce the lifetime of the SOFC due to electrode poisoning. In order to reduce or even prevent these phenomena, coating of the steel’s surface with a conductive material, such as spinel type oxides based on the Mn - Co system is one possible solution.

In this work, oxides with spinel structure were produced by thermal oxidation of metallic thin films from the Mn - Co - Fe system. Thermodynamic and phase stability calculations were performed in order to determine the suitable annealing environment. It was shown that the annealing atmosphere necessary to convert the Mn - Co and Mn - Co - Fe metallic films to oxides with spinel structure should contain an high amount of O₂, with partial pressures close to atmospheric pressure.

The metallic films (0.3 µm) with compositions: Mn₆₇Co₃₃, Mn₅₀Co₅₀, Mn₅₀Co₃₂Fe₁₇ and Mn₃₃Co₆₇ were deposited by magnetron co-sputtering on oxidised silicon wafers. The oxidation of metallic coatings was studied as a function of annealing temperature (600 - 800 °C), annealing time (15 - 60 min) and atmosphere (O₂ and ambient air) revealing that, after a suitable heat treatment, the thin metallic coatings can be successfully converted to oxides. Solely spinel structures were obtained for the Mn₃₃Co₆₇, Mn₅₀Co₅₀ and Mn₅₀Co₃₂Fe₁₇ compositions when annealed in O₂ independently of the annealing temperature and time. The Mn₆₇Co₃₃ composition led to spinel structure only when annealed for 1 h at 800 °C. Other oxide phases (e.g. Mn₂O₃ and CoMnO₃) formed along with the spinel phase for this composition at lower temperatures due to the large amount of Mn present. Based on the results obtained in O₂ environment, samples were also annealed in ambient air for 1 h at 800 °C. After this annealing, pure spinel phases were obtained only for the Mn₃₃Co₆₇, Mn₅₀Co₅₀ and Mn₅₀Co₃₂Fe₁₇ compositions [93, 94], whereas a Mn-rich secondary phase was detected along with the spinel phase for Mn₆₇Co₃₃.
Before starting the investigations of coatings on steel substrate (ZMG232L Hitachi Metals Ltd.), the steel itself was annealed for different durations at 800 °C in an atmosphere simulating the cathodic-side (ambient air) and anodic-side (97 % H₂ and 3 % H₂O) of a SOFC. ZMG232L stainless steel develops a duplex (Mn, Cr)₃O₄/Cr₂O₃ oxide scale independently of the partial pressure of O₂, when annealed at 800 °C. The scale grown in reducing environment is thinner than the one grown in oxidising environment, due to the lower O₂ availability for the former. Also, the scales grown in different environments have different surface microstructures, with crystals in the case of high amounts of O₂ and whiskers and ridges for low amounts of O₂. ASR measurements performed in ambient air revealed that the oxide scale follows a parabolic growth, governed by diffusion, with the ASR value being around 13 mΩ·cm² after 601 h annealing and with the oxide scale thickness having approximately 2.2 µm.

Thin films with Mn₅₀Co₅₀ and Mn₅₀Co₃₃Fe₁₇ compositions and 0.3 µm initial thickness deposited on the bare stainless steel did not present protective properties regarding ionic transport (e.g. Cr and Mn) from the substrate during long time annealing at high temperature in oxidising atmosphere. The growth of substrate oxide underneath the thin coatings led to stress in the layers that were partially destroyed after long time annealing to high temperature in oxidising atmosphere [100, 109, 110]. High ASR values were measured for these samples (40 - 59 mΩ·cm²) and secondary oxide phases (i.e. Mn₂O₃) were detected along with the spinel phase. Increasing the thickness of the metallic coatings to 1 µm resulted in the decrease of the ASR values for the Mn₅₀Co₅₀ coating (33 mΩ·cm²), that also showed blocking properties regarding Cr diffusion. The Mn₃₃Co₃₃Fe₁₇ coating still presented high ASR (62 mΩ·cm²), probably due to the very rough surface of the oxide, and the blocking properties were also poorer than the properties of Mn₅₀Co₅₀, as small amounts of Cr were detected at the surface. Increasing the thickness had a beneficial effect on the stability of the coatings as well, which were not destroyed after the long time annealing. However, the thicker coatings did not hinder the Mn transport from the substrate and secondary Mn₂O₃ oxide phases were detected for both coatings, together with the appearance of grain deformation. Independently of the thickness and composition, the ASR versus √t dependence was not linear. This indicates that either the growth of the substrate oxide underneath the coating was not diffusion-controlled and faster paths were available for the ionic transport and/or other oxide phases are formed having higher electrical resistivity. The thickness of the (Mn, Cr)₃O₄/Cr₂O₃ oxide scale grown underneath the coatings was approximately 4 µm.

The annealing studies performed on the steel substrates revealed that 100 h annealing at 800 °C in ambient air is a suitable heat treatment in order to form a continuous spinel layer on top of the oxide scale developed on the surface. Coatings deposited on 100 h pre-annealed steel showed improved properties when compared with the coatings deposited on bare steel. Thick Mn₅₀Co₅₀ and Mn₅₀Co₃₃Fe₁₇ coatings had low ASR values (17 mΩ·cm²), no other secondary oxide phases (e.g. Mn₂O₃ and/or Fe₂O₃), no changes in the grains structure and no Cr
diffusion throughout the coatings during the duration of the experiments [109]. The thickness of the (Mn, Cr)$_3$O$_4$/Cr$_2$O$_3$ substrate oxide grown underneath the coatings was 2.2 µm.

Decreasing the thickness of the coatings led to important differences in the behaviour of the coatings. Both compositions showed low ASR values (15 - 19 mΩ·cm$^2$) and also low thickness of the (Mn, Cr)$_3$O$_4$/Cr$_2$O$_3$ oxide scale grown underneath (2.2 µm). However, the Mn$_{50}$Co$_{50}$ coating showed no Mn$_2$O$_3$ oxide phase and lower Cr enrichment than the Mn$_{50}$Co$_{33}$Fe$_{17}$ coating [100]. For the Mn$_{50}$Co$_{33}$Fe$_{17}$ coating, the Cr content was high and the Mn$_2$O$_3$ phase led to changes in the grain structure. From the present study it seems that the lower limit of the coatings thickness was reached.

The studies performed on thin and thick Mn - Co and Mn - Co - Fe coatings deposited on pre-annealed ZMG232L stainless steel indicate that thicker coatings show better protection regarding Cr diffusion, but still the question remains if these coatings would be still protective if the exposure is longer than 500 h. The enhanced ionic transport from the substrate into the thin Mn$_{50}$Co$_{33}$Fe$_{17}$ coating suggest that this coating it would not be suitable for long time applications. On the other hand, both thin and thick Mn$_{50}$Co$_{50}$ coatings showed superior properties, therefore this coating was chosen for long time testing in order to verify its properties regarding both Mn and Cr ions transport. The 2 000 h annealed 1 µm Mn$_{50}$Co$_{50}$ coating deposited on processed ZMG232L proved that the coating has blocking properties regarding Cr diffusion, it is well adherent to the substrate and low ASR values (28 mΩ·cm$^2$) can be achieved. Also Mn transport from the substrate into the coating is indeed hindered by pre-annealing the substrates before the Mn$_{50}$Co$_{50}$ coatings deposition. Therefore, it can be concluded that 100 h annealed ZMG232L + 1 µm metallic coating with the composition Mn : Co = 50 : 50 (at.%) produced by co-sputtering is a promising substrate for SOFC interconnects. Nevertheless, there are factors that can influence the behaviour of the interconnects: tens of thousands h annealing at high temperature, the presence of the cathode, as well as the annealing in dual atmospheres, therefore this work opens new perspectives and new research opportunities for further studies.