

Effect of nano-layered ceramic coatings on the electrical conductivity of oxide scale grown on ferritic steels

S. Chevalier · G. Caboche · K. Przybylski ·
T. Brylewski

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Abstract The electrical conductivity of a coated and uncoated model Fe-30Cr ferritic steel was studied between 973 and 1,073 K. The ASR values decreased with temperature increase. The application of a nano-structured ceramic coating made of yttria on the surface of the steel induced a decrease of the ASR values, especially at 1,073 K, which is the operating temperature for Intermediate Temperature Solid-Oxide Fuel Cells. The ASR value of the yttria-coated alloy is $9.3 \text{ m}\Omega \text{ cm}^2$ compared to $37.8 \text{ m}\Omega \text{ cm}^2$ determined on the uncoated steel after 100 h at 1,073 K in air. The estimated value of the ASR parameter after 10,000 h is encouraging, as it is limited to $17 \text{ m}\Omega \text{ cm}^2$. The oxidised surfaces were characterised by scanning electron microscopy and X-ray diffraction. The results were compared with the literature.

Keywords Fuel cells · Films · Y_2O_3 · Perovskite · Electrical conductivity

1 Introduction

Interconnects are of major importance among the components constituting Solid-Oxide Fuel Cells (SOFC) because they collect the electrons and guarantee good functioning

of the cells. The interconnects have to fulfill a certain number of criteria, such as excellent electrical conductivity, good chemical stability, low permeability for oxygen and hydrogen, a thermal expansion coefficient (CTE) comparable to those of the other components of the cell (classically the cathode made of $(\text{La,Sr})\text{MnO}_3$ based compounds, the anode made of Ni-YSZ cermets and the electrolyte composed of YSZ) [1, 2], as well as excellent oxidation, sulphidation and carburisation resistances [3, 4]. The decrease in SOFC operating temperature from high (1,273 K) to intermediate temperatures (1,073 K) makes it possible to replace classical ceramics (mainly LaCrO_3 perovskite compounds [5]) by metallic interconnects. This change yields several advantages such as lower price, better mechanical properties and then ease of shaping, but requires choosing adapted metals or alloys having good resistance to high temperature oxidation, good behaviour in reducing atmospheres and good electrical conductivity.

Review papers [6, 7] clearly show that chromia-forming steels are among the better candidates for interconnect materials because they form a protective chromia layer under high temperature oxidising atmospheres. Nevertheless, the electrical conductivity of Cr_2O_3 scale is poor, and does not correspond to that required for SOFC applications (typically between 25 and $50 \text{ m}\Omega \text{ cm}^2$ [6]). The second problem encountered with chromia is its potential transformation into volatile chromium species, such as CrO_3 or $\text{CrO}_2(\text{OH})_2$ leading to the loss of its protectiveness and degradation of the fuel cell [3, 8, 9]. Tests performed on ferritic steels in dual atmosphere (one side under air and the other side under $\text{H}_2 + 3\% \text{ H}_2\text{O}$) clearly showed that the scale growth was significantly different from scale growing in a single atmosphere [10]. Oxygen reacts with the interconnect to form oxides whereas hydrogen can migrate across the interconnect as an interstitial element inside the

S. Chevalier (✉) · G. Caboche
Institut Carnot de Bourgogne, UMR 5209 CNRS, Université de Bourgogne, 9 Avenue Savary, BP 47870, 21078 Dijon cedex, France
e-mail: sebastien.chevalier@u-bourgogne.fr

K. Przybylski · T. Brylewski
Faculty of Materials Science and Ceramics, Department of Solid State Chemistry, AGH University of Sciences and Technology, Krakow, Poland

metal, causing embrittlement and leading to the detrimental presence of hydrogen at the metal-oxide interface as well as in the oxide scale on the air side [11].

In order to guarantee durability and reliability, chromia-forming alloys require bulk or surface modification [4]. Specific alloys have been developed in order to limit the evaporation of chromium oxides and/or hydroxide species by producing thermally grown conductive layers enriched in spinel phases [12–14]. The formation of iron substituted $\text{Mn}(\text{Cr},\text{Fe})_2\text{O}_4$ instead of Cr_2O_3 or MnCr_2O_4 was found to improve the conductivity of oxidised interconnects [15] and to decrease the evaporation of chromium [16]. A second eventuality consists in modifying their surface by applying surface treatment, able to balance the two opposed properties: corrosion resistance and electrical conductivity [6, 17–21], by improving the oxide scale adherence, the resistance to thermal cycling and by decreasing the resistivity of the scale [11]. A previous study showed that it was possible to form perovskite compounds from reactive element oxide (REO) deposited by metal organic chemical vapor deposition (MOCVD) on chromia-forming steels [22]. Ceramic coatings also lead to better oxidation resistance at high temperature, since they decreased the oxidation rate and increased the oxide scale adherence [23, 24].

The aim of this work was to estimate the applicability of Fe-30Cr model alloys and Fe-30Cr alloys subjected to surface modification by Y_2O_3 coating, using the MOCVD method for construction of metallic interconnects in planar type SOFC intended for operation at 1,073 K. The reason why a model Fe-30Cr alloy was chosen was to investigate the effect of the ceramic coating on an alloy containing no minor elements. The next step in the study will be to test the proposed ceramic coating on commercial alloys, such as Crofer 22 APU (ThyssenKrupp VDM, Werdohl, Germany), ZMG 232 (Hitachi Metals, Tokyo, Japan) as well as the ODS-alloys IT-10, IT-11 and IT-14 (Plansee, Reutte, Austria), which were specifically developed for interconnects in SOFC applications. The present study is focused on the effect of the application of a nano-structured ceramic film formed by MOCVD on the area specific resistance (ASR) of thermally grown oxide layers formed on the cathode side (air).

2 Experimental procedure

The alloy studied in this work was a model ferritic alloy Fe-30Cr (wt%) which contained no minor elements. The samples were cut in discs of 1 cm diameter and about 1-mm-thick. Prior to oxidation or deposition, the Fe-30Cr samples were polished from 240 grit silicon carbide up to 1 μm with diamond paste. They were then cleaned in ethanol in an ultrasonic bath and dried.

The coatings of reactive element oxides were applied on the Fe30Cr alloy by the Metal Organic Chemical Vapour Deposition (MOCVD) technique. β -diketonates were used as metallo-organic precursors [25]. This technique enables thin oxide films about 200-nm-thick to be produced. Transmission electron microscopy (TEM) and Atomic Force Microscopy (AFM) analyses carried out on similar Nd_2O_3 films prepared by MOCVD showed that the ceramic coatings were composed of very small crystallites of the reactive element oxide (30–40 nm) [26].

For high temperature electrical resistance measurements of the samples as potential materials for metallic interconnect, measuring probes enabling measurements in different atmospheres (air, H_2 - H_2O or CH_4 - H_2O) were used. The measurements of electrical resistance were conducted by the dc two-probe method using an outer source of current. The resistance was determined on the basis of Ohm's law. Figure 1 shows a schematic diagram of the measurement of the sample resistance. Both surfaces of the pre-oxidized samples (1,073 K, 24 h, air), having 8 mm diameter and 0.7-mm-thickness were covered by platinum paste (Heraeus) followed by placing platinum meshes of surface area 25 mm^2 on top of the pastes. In these measurements the mesh played the role of current collector. The sample prepared in this sandwich system was placed between two plane Pt electrodes and the voltage drop was measured at dc 10 mA current using a current supply (JOTA). The current drop on the sample was measured using a HP digital multimeter (34401 A) with error not exceeding 0.3%. Each measurement of the electrical resistance was conducted and verified for reproducibility at constant temperature in a short time to avoid further oxidation of the samples.

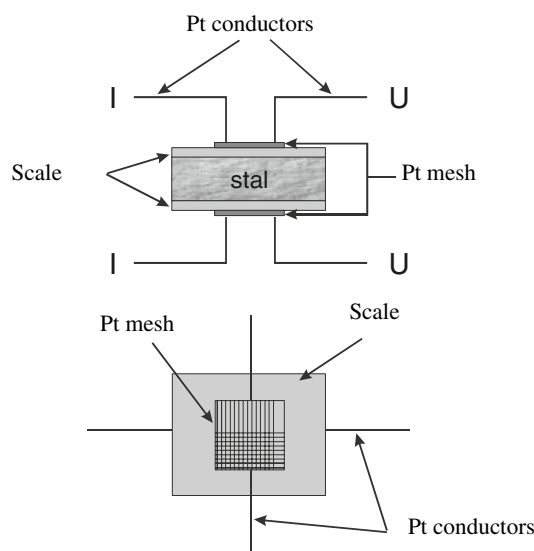


Fig. 1 Schematic diagram of the sample resistance measurement

On account of the progress of scale growth due to the oxidation of coated and uncoated Fe-25Cr alloy in the course of the ASR measurements, an attempt was made to reduce as much as possible the duration of the measurements as suggested elsewhere [27]. Thus, the sample resistance was recorded at a given temperature (between 973 and 1,073 K) every 10 min. The temperature was then increased by 25 K and the sample was equilibrated at this increased temperature for 1 h.

To calculate the area specific resistance (ASR) of the samples, and thereby to test its applicability for the metallic interconnect construction, the following relation was used:

$$(ASR)^2 = \frac{(M_{Cr_2O_3})^2 \times k_p}{(3 \times M_O \times \rho_{Cr_2O_3})^2 \times \sigma^2} \times t \tag{1}$$

where: $M_{Cr_2O_3}$ molar mass of chromium oxide (151.99 g mol⁻¹), k_p parabolic rate constant of oxidation (g² cm⁻⁴s⁻¹), M_O molar mass of oxygen (15.99 g mol⁻¹), $\rho_{Cr_2O_3}$ density of chromium oxide (5.225 g cm³), σ electrical conductance of the sample (Ω⁻¹ cm⁻¹) and t oxidation time (86,400 s = 24 h). A more direct approach would have consisted in applying the simple relationship $ASR = R \times A$, with R the oxide scale resistance (ohm) and A its area (cm²). However, the use of relationship (1) is a more accurate approach.

The parabolic rate constants, k_p , were collected from a previous study performed on the same systems: uncoated Fe-30Cr and Y₂O₃-coated-Fe-30Cr [28]. They were determined from the slopes of the plots $\Delta m/A$ vs. $t^{1/2}$. The values were 1.4×10^{-12} (g² cm⁻⁴ s⁻¹) for uncoated alloy and 1.3×10^{-13} (g² cm⁻⁴ s⁻¹) for coated alloy, respectively. These values are close to those found in the literature. For commercial alloys, minor element additions could slightly modify the k_p values, especially when MnCr₂O₄ spinel is formed [29].

The oxidized surface morphologies were observed using scanning electron microscopy (SEM) and energy dispersive X-ray analysis. Surface and fraction cross-sections of the oxidized samples were observed by SEM. The oxide phases were identified by X-ray diffraction using K α copper radiation ($\lambda = 0.154$ nm).

3 Results

3.1 Electrical conductivity

The electrical resistivities were measured as a function of temperature for Fe-30Cr pure alloys and Fe-30Cr alloys coated with Y₂O₃. The resistance decreases with temperature. The resistance of the coated samples is always lower than that of the uncoated specimen. The results of the ASR

calculations are listed in Table 1. The ASR parameter is always lower for the Y₂O₃-coated steels than for the uncoated alloys. The gap between the ASR values increases with temperature.

Figure 2 is an Arrhenius plot of the ASR changes as a function of temperature for Fe-30Cr pure alloys and Fe-30Cr alloys coated with a Y₂O₃ layer. The activation energy of the conductivity calculated from the slope of a log ASR/T vs. 1/T plot (Fig. 2) for the uncoated Fe-30Cr alloy and coated Fe-30Cr alloy are 0.15 and 0.19 eV, respectively.

Figure 2 indicates that the scale, formed on Fe-30Cr alloy subjected to surface modification with Y₂O₃ coating using the MOCVD method and pre-oxidised in air for 24 h at 1,073 K, is characterized by a lower value of ASR in comparison with Fe-30Cr pure alloy. This may be connected with the small thickness of the scale adhering to the coated alloy.

3.2 Oxide scale characterization

The SEM micrographs did not reveal any essential differences in the grain size for both examined scales (Figs. 3 and 4). The chemical composition of the scale, determined by EDS, is composed of Cr and O on both samples. It is possible only to see differences in the grain shape of the chromia scale. The chromia scale formed on the uncoated Fe-30Cr alloy is dense and built of well crystallized grains having a regular shape (Fig. 3a, b). The dimension of these grains is about 0.4 to 3 μm.

Cr₂O₃ grains formed on the yttria-coated alloy have oval shapes with sizes from about 0.7 up to 4 μm, which create agglomerates (Fig. 4a, b). Morphological observations of the cross-sections of the scales on Fe-30Cr alloy were carried out by SEM. Figure 5 shows the SEM fracture cross-section of the chromia scale formed on the uncoated Fe-30Cr alloy. The thickness of the scale is about 2 μm. As can be seen from the micrograph, the chromia scale shows a tendency to deform and contains voids and cavities near the metal-scale interface. The scale also shows a buckled appearance.

Table 1 ASR parameters determined on uncoated and Y₂O₃-coated alloys between 973 and 1073 K

Temperature/K	ASR/Ω cm ²	
	Uncoated alloy	Coated alloy
973	50.8 × 10 ⁻³	13.7 × 10 ⁻³
998	47.9 × 10 ⁻³	12.7 × 10 ⁻³
1,023	44.9 × 10 ⁻³	11.6 × 10 ⁻³
1,048	41.5 × 10 ⁻⁵	10.5 × 10 ⁻³
1,073	37.8 × 10 ⁻³	9.3 × 10 ⁻³

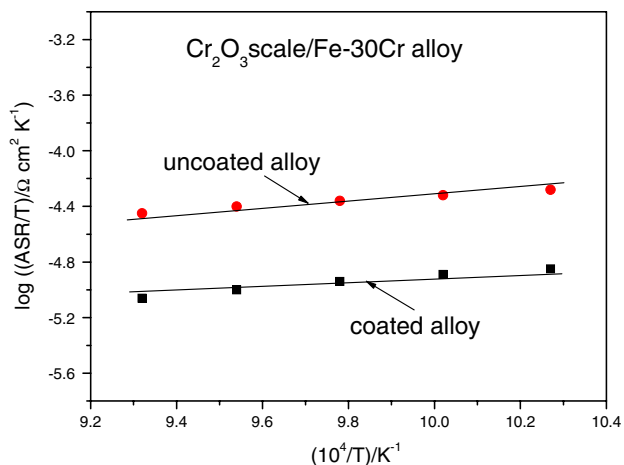


Fig. 2 Temperature dependence of ASR determined on Fe-30Cr pure alloys and Fe-30Cr alloys with Y_2O_3 ceramic coating in air atmosphere

The scale formed on the yttria-coated alloy is thinner than that grown on the uncoated alloy; it is around 1- μm -thick after 24 h at 1,073 K (Fig. 6). The micrograph exhibits no cavities near the metal-oxide interface and no buckling is seen. The scale appears to be adherent to the underlying substrate.

Investigations of the phase composition of the scale formed on the coated and uncoated Fe-30Cr alloy by XRD have revealed the presence of chromia only. Compared with the uncoated alloy, the diffraction pattern of the coated alloy reveals the presence of peaks corresponding to the substrate; this observation shows the smaller thickness of the scale formed on the coated alloy in comparison with the thickness of scale grown on uncoated alloy. The use of a glancing angle of 1° allowed the detection of $YCrO_3$ peaks on the coated surfaces [28].

4 Discussion

The results obtained from ASR, SEM coupled with EDS and XRD indicate the benefits of surface treatment on the surface of a model ferritic steel. The values of the ASR parameter are always lower on the Y_2O_3 -coated Fe-30Cr steel than on the uncoated alloy. At 1,073 K, which is the common temperature proposed for IT-SOFC, the ASR value, 37.8 and 9.3 $\text{m}\Omega \text{ cm}^2$ for the coated and uncoated Fe-30Cr steels, respectively, are in the range of the target values 25–50 $\text{m}\Omega \text{ cm}^2$ [6]. The ASR value of the yttria-coated sample appears lower than the values obtained for a $La_{0.6}Sr_{0.4}CoO_3$ coated Fe-16Cr, which were 45 $\text{m}\Omega \text{ cm}^2$ under H_2 - H_2O atmosphere and 20 $\text{m}\Omega \text{ cm}^2$ in air [18]. The value of ASR on the yttria-coated Fe-30Cr is comparable to that found for a 430 SS coated with a Mn-Co-O spinel, 2.5 $\text{m}\Omega \text{ cm}^2$ after 60 h at 1,073 K followed by additional

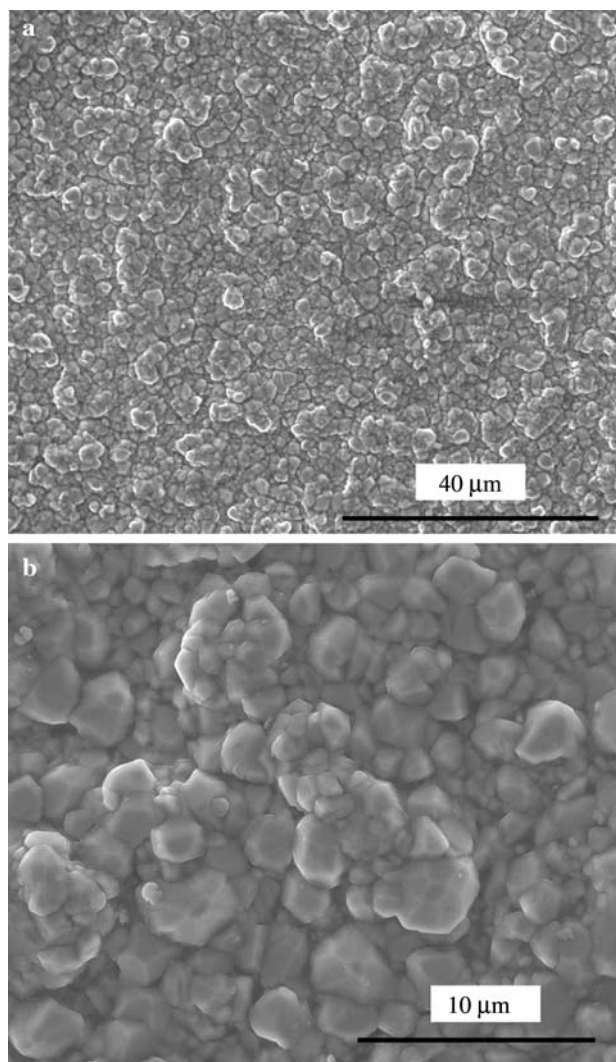


Fig. 3 **a** SEM micrograph of chromia scale formed on uncoated Fe-30Cr alloy after oxidation at 1,073 K in air for 24 h and **b** higher magnification

cyclic oxidation at 1,123 K for 120 h [30]. Nevertheless, the operating duration of interconnects in SOFC devices is longer than the duration of the tests proposed in the present paper. It is then necessary to estimate their behavior after 1,000 h of exposure under oxidizing atmospheres. For Fe-25Cr steels oxidized in air at 1,073 K, the estimated ASR value for 10,000 h was 0.78 $\Omega \text{ cm}^2$, which was too high for use as interconnect. The ASR value for a Fe-26Cr-1Mo alloy oxidized for 48 h at 1,073 K was 15 $\text{m}\Omega \text{ cm}^2$, whereas it reached a predicted value of 200 $\text{m}\Omega \text{ cm}^2$ after 1,000 h. [31]. The estimation of the ASR value on our uncoated samples shows that the ASR value would reach 680 $\Omega \text{ cm}^2$ after 10,000 h at 1,073 K, whereas the ASR value estimated on the Y_2O_3 -coated steel would be 0.17 $\Omega \text{ cm}^2$. This means that, after 10,000 h of service, the electrical conductivity of the scale grown on the ceramic-

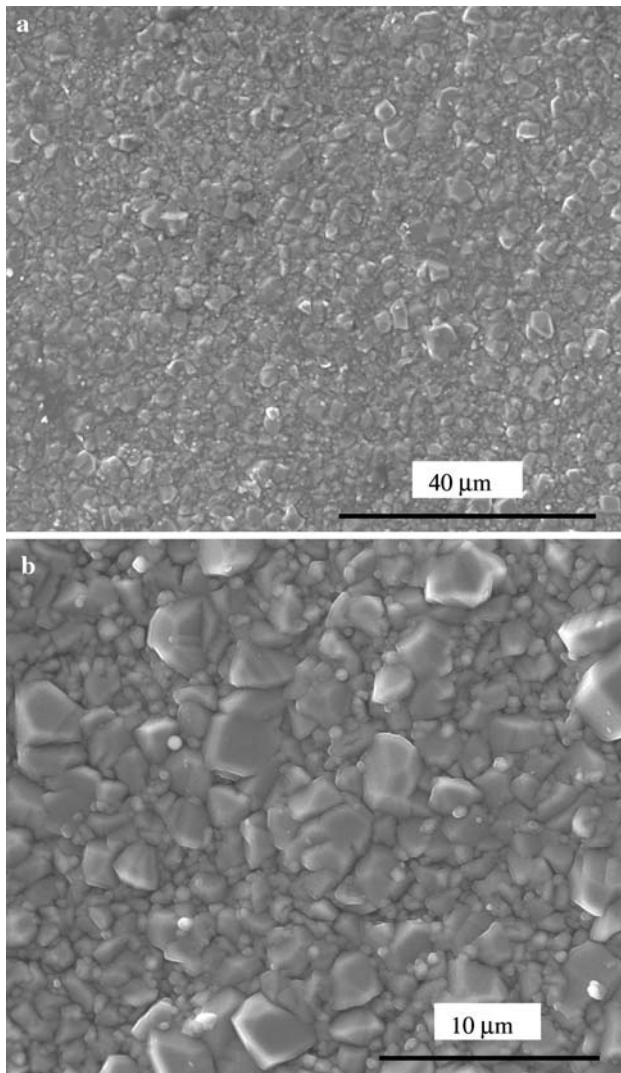


Fig. 4 **a** SEM micrograph of chromia scale formed on Y_2O_3 -coated Fe-30Cr alloy after oxidation at 1,073 K in air for 24 h and **b** higher magnification

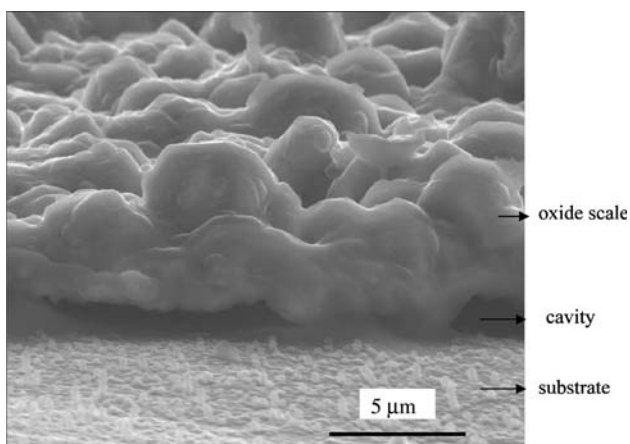


Fig. 5 Fracture cross-section of chromia scale formed on uncoated Fe-30Cr alloy after oxidation at 1,073 K in air for 24 h

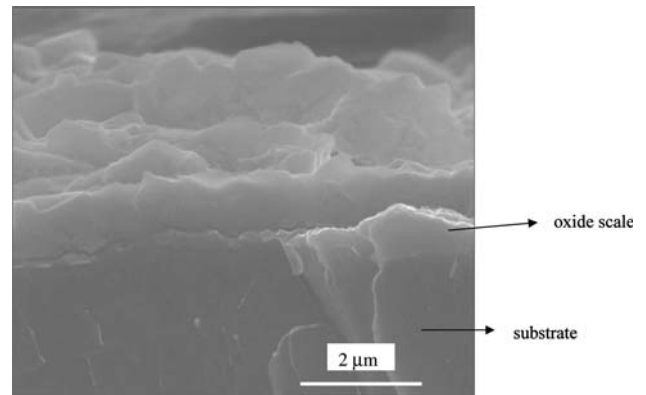


Fig. 6 SEM micrograph of chromia scale fracture cross-section formed on Y_2O_3 -coated Fe-30Cr alloy after oxidation at 1,073 K in air for 24 h

coated alloy would be drastically reduced compared to that of the uncoated alloy. Nevertheless, this is true only if the scale growth is the same as that observed after 100 h at 1,073 K. The formation of $YCrO_3$ perovskite phase on the yttria-coated alloys is responsible for the improvement in electrical conductivity, compared to chromia scale.

The linear plots of $\log ASR/T = f(1/T)$ indicate that conductance of the electric current takes place in accordance with small polaron movement in the chromium oxide crystal lattice. The values of the activation energies determined for the uncoated Fe-30Cr alloy and coated Fe-30Cr alloy (0.15 and 0.19 eV, respectively) are lower than values obtained for pure Cr_2O_3 scale thermally grown on the surface of a pure Cr substrate or on sintered chromia (0.55 eV [32] and 0.6 eV [33]). The activation energy was 0.9 eV in the case of a Cr_2O_3 scale grown on a Fe-based alloy [27, 34], indicating that the conductivity was dominated by impurities in the scale.

A second aspect has to be considered: the pre-oxidation of the coated samples for 24 h at 1,073 K leads to the formation of very little perovskite phase, $YCrO_3$. A pre-oxidation at higher temperature (1,273 K) is envisaged in order to form a complete perovskite layer, able to give better ASR values.

5 Conclusions

Surface modification of a ferritic steel by the deposition of Y_2O_3 nano-ceramic layer using MOCVD, contributes considerably to improvement in the chemical resistance of the alloy and also of its electrical properties. The ASR values decrease drastically between 973 and 1,073 K but remain lower on the yttria-coated alloys. The estimated value of the ASR after 10,000 h is very encouraging, as it is limited to $17 \text{ m}\Omega \text{ cm}^2$. The improvement in the ASR parameter is due to the thinner oxide scale and to the

formation of a YCrO_3 perovskite phase which has better electrical conductivity than chromia.

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