

Islamic Azad University
Marvdasht Branch

Journal of Physical Chemistry and Electrochemistry

Journal homepage: <http://journals.miau.ac.ir/jpe>

Decrease of Electrical Conductivity Activation Energy of Co-coated AISI 430 Alloy for the Application of SOFCs

Hadi Ebrahimifar^a and Morteza Zandrahimi^{a,*}^aDepartment of Metallurgy and Materials Science, Faculty of Engineering, Shahid Bahonar University of Kerman, Kerman, Iran

Abstract

The application of conductive coatings on ferritic stainless steel can decrease electrical conductivity. The aim of this research was to investigate the electrical conductivity of cobalt coated AISI 430 ferritic stainless steel by pack cementation technique. Coated coupons were analyzed using scanning electron microscopy (SEM). Electrical conductivity of the coated substrates was measured as a function of temperature by oxidizing the samples from room temperature to 700 °C. Also electrical conductivity has been measured as a function of oxidation time during isothermal oxidation at 700 °C. Results showed the increase of temperature caused to the decrease of electrical conductivity and also, the coating layer converted to cobalt spinels during annealing in isothermal oxidation. The formation of $MnCo_2O_4$, $CoCr_2O_4$, $CoFe_2O_4$ and Co_3O_4 spinels improved electrical conductivity activation energy of coated substrates (0.03 eV) compared to uncoated substrates (0.039 eV).

Keywords: Cobalt, AISI 430, Electrical conductivity activation energy, Solid oxide fuel cell

1. Introduction

Solid oxide fuel cells (SOFCs) have recently attracted tremendous interest because of their high efficiency, low pollution emission, and relatively flexible fuel choice. Recent progress in the development of planar intermediate-temperature SOFCs has made it possible to use metallic alloys as the interconnect material. Several chromia-forming ferritic stainless steels, such as Crofer 22 APU, UNS 430 and ZMG232 are particularly promising, as they offer the advantages of low raw material

cost, excellent formability, high electrical and thermal conductivity, good oxidation resistance, and thermal expansion match with adjacent cell components. However, there are two major challenges associated with these ferritic alloys, including increase in electrical resistance over time due to continuous oxidation at elevated temperatures and evaporation/migration of the Cr species from the interconnect alloy into the cathode, both of which lead to severe degradation in cell performance. Protective and conductive oxide coatings have been proposed to reduce the Cr volatilization of the Cr-containing interconnect alloys by acting as a barrier for Cr migration/transport [1-7].

*Corresponding author

Tel: +98 341 2114053, Fax: +98 341 2111865

E-mail: m.zandrahimi@mail.uk.ac.ir

Most recent researches, however, have concentrated on the application of protective/conductive coatings. Numerous techniques have been developed to apply coatings to ferritic stainless steels. These include slurry coatings [8-11]. Anodic electrodeposition [12], cathodic electrodeposition of particular metals or alloys, followed by annealing/oxidation in air and pack cementation [13-16]. The latter method has been attracting attention due to its low cost, ease of fabrication, good adhesion between the deposited coating and substrate and extensive application.

The objective of the current work was to investigate the electrical conductivity activation energy of cobalt-coated AISI 430 specimens by pack cementation technique.

2. Experimental procedure

amples of AISI 430 stainless steel, measuring 10 mm × 5 mm × 2 mm with chemical composition of 17.4% Cr, 0.92% Mn, 0.85% Si, 0.12% C, 0.02% S, and 0.03% P with Fe as remaining were used as substrates. Specimens were polished from 320-grit paper up to 1200-grit, ultrasonically cleaned in ethanol and dried. In order to deposit cobalt onto the substrate, pack cementation method was employed. Co, Al₂O₃ and NH₄Cl powder were used as powder mixture in average size of 1 μm, 70-80 μm and 240 μm. The optimized conditions for coating of cobalt onto the surface of AISI 430 stainless steel by pack cementation were identified: 10% wt. Co, 1% wt. NH₄Cl, 89% wt. Al₂O₃ as powder mixture and annealing at 800 °C for 3 h at presence of Ar gas. After pack cementation treatment, the samples were removed from the pack and ultrasonically cleaned in ethanol to remove any embedded pack material. Electrical conductivity measurement of the oxidized samples was accomplished by employing the set-up shown in Figure 1. Platinum wires were spot welded to one side of two identical polished samples to provide electrical connections. To avoid alloy-to-alloy adhesion and erroneous results, platinum wire welded specimens were pre-oxidized for 24 h at 700 °C. No conductive paste, which may

affect the oxidation mechanism, was applied between the two samples. A constant current density of 500 mA cm⁻² was applied and the voltage was recorded every 30 minutes. An ammeter and a voltmeter were employed for this purpose. The data were used to calculate the conductivity according to Ohm's law and the electrical conductivity as a product of the conductivity and surface area. In order to measure the resistance contribution from the junctions, wires and the alloy, two platinum wires were spot welded to the sides of a single AISI 430 specimen and the resulting resistance was subtracted from the original test results. Electrical conductivity was measured as a function of different temperatures (400-700 °C) for 200 h and as a function of time at 700 °C. The above mentioned tests were run at an electric box furnace and static air.

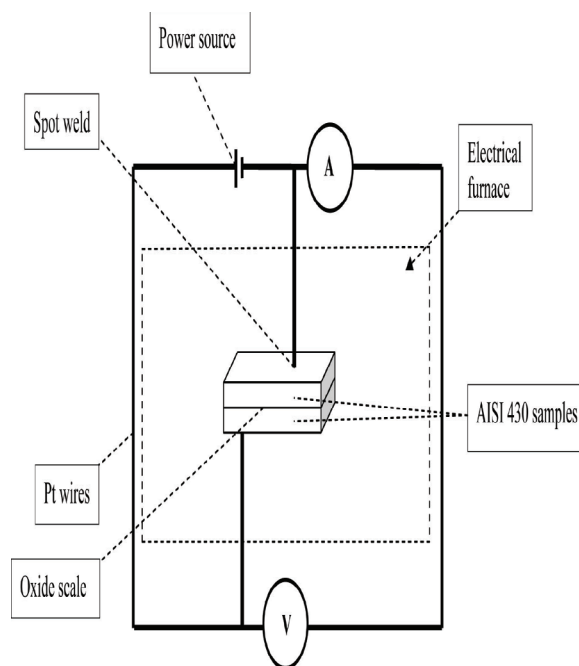


Fig. 1. Instruments consist of voltmeter, ammeter and constant current density for measuring the electrical conductivity of oxide scale

Cross-section microstructure and chemical composition of coated specimens were analyzed using scanning electron microscopy (SEM) (Camscan MV2300) with energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) was used to identify phases formed in the surface layer of as-coated and oxidized specimens with a Philips X'Pert High Score diffractometer using Cu K α ($\lambda =$

1.5405 Å).

3. Results and discussion

3.1. Coating of substrate

Figure 2 shows cross-sectional SEM image (Figure 2a) and EDS line scan (Figure 2b) of a coated sample. The identified phases in XRD pattern included $MnCo_2O_4$ and $CoCr$ [17].

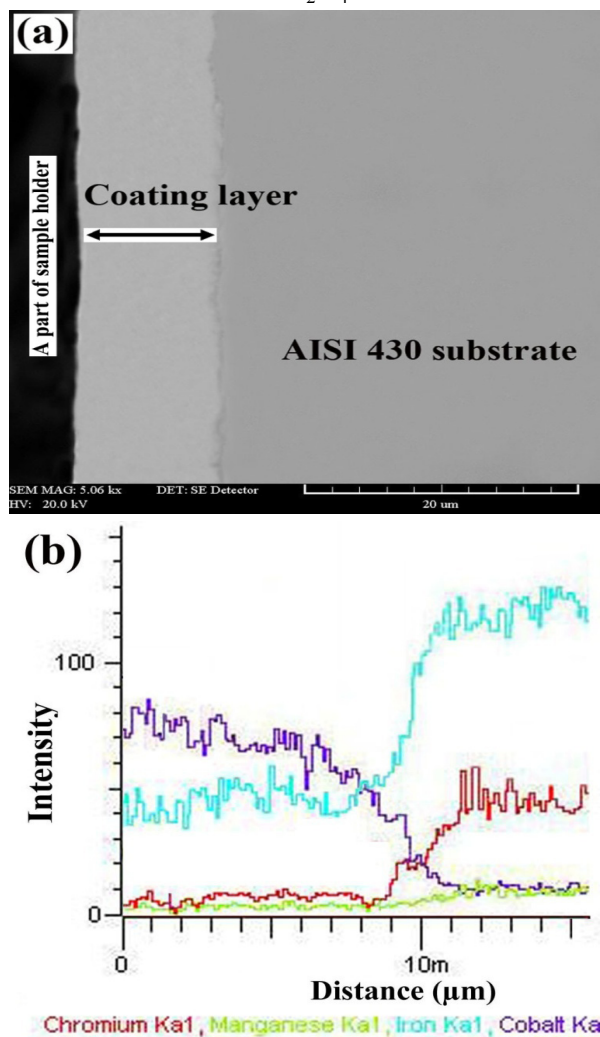


Fig. 2. SEM cross section image of coating (a) and EDS line scan (b)

3. 2. Evaluation of electrical conductivity as a function of time

The electrical conductivity for coated and uncoated AISI 430 stainless steel, as a function of time were plotted in Figure 3. Electrical conductivity values for uncoated substrates decrease with oxidation time and approach to a value of 32 S.cm⁻¹ after 200

h isothermal oxidation. Coated specimens however, exhibited a very low resistance (128 S.cm⁻¹) after 200 h. Fig. 4 shows XRD pattern of uncoated (Fig. 4a) and coated (Fig. 4b) specimens after 200 h isothermal oxidation. In XRD pattern of bare substrate $(Mn,Cr)_3O_4$ spinel, chromia and silica are observed. The presence of $(Mn,Cr)_3O_4$ spinel on the surface of bare substrate refers to ferritic stainless steels that normally containing small levels of Mn [18,19].

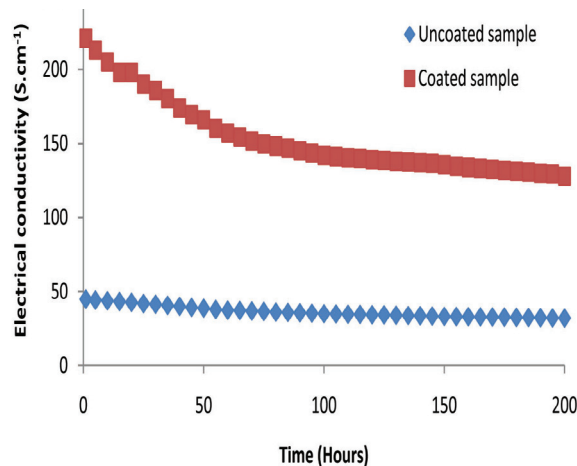


Fig. 3. Electrical conductivity values as a function of time for uncoated and coated samples in isothermal oxidation

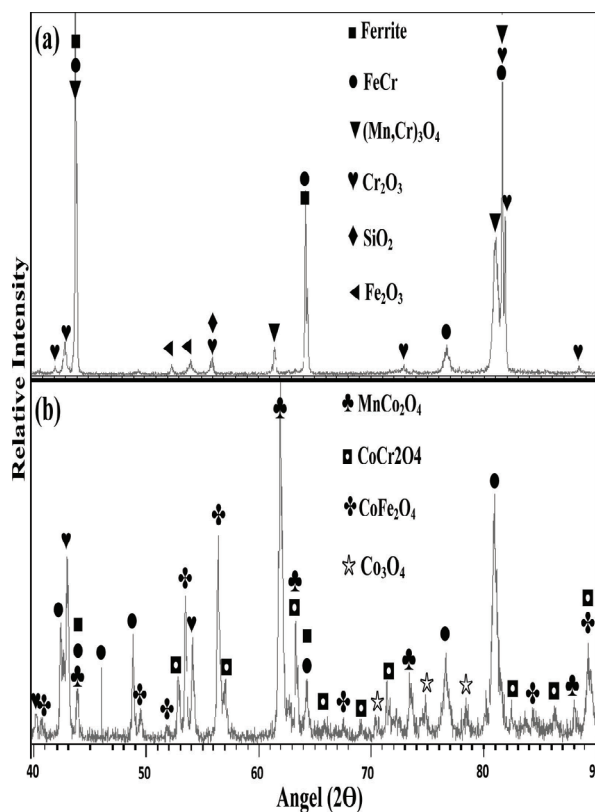


Fig. 4. XRD pattern of (a) uncoated and (b) coated specimens after 200 h isothermal oxidation at 700 °C.

There are several factors can contribute to the increased resistance. The primary factor is the growth of the oxide scale [20]. The conductivities of both $(\text{Mn,Cr})_3\text{O}_4$ spinel and chromia are considerably smaller in comparison with the metallic substrate [21]. An increase in the thickness of the oxide scale, therefore, proportionally decreases the electrical conductivity. The formation of an insulating silica layer as the result of interfacial segregation of Si is another important factor which can negatively affects the electrical conductivity of steels containing Si. There are also other contributions to increased electrical resistance that are related to the metal/oxide scale interface. Interfacial imperfections, including voids and cavities as well as impurity segregation, reduce the scale-to-metal adhesion and actual surface area of intimate contact between the metal and oxide scale and, consequently, increase the interconnect electrical resistance [20,21]. The spalled surface and the probable existence of cavities in the bare substrate reduce the actual contact surface area between the alloy and scale [22-25].

The formation of MnCo_2O_4 , CoCr_2O_4 , CoFe_2O_4 and Co_3O_4 spinels during oxidation improved the electrical conductivity. Electrical conductivity of these spinels is remarkably higher than $(\text{Mn,Cr})_3\text{O}_4$ spinel and chromia. Several factors can contribute to the improved electrical conductivity for the coated substrate over uncoated ones. These include the higher electronic conductivity of the scale consisting of cobalt spinels, the absence of silica phase and improved the adhesion of oxide scale.

3. 3. Evaluation of electrical conductivity activation energy

In order to investigate the influence of temperature on the electrical conductivity, it was measured at different temperatures (from room temperature to 700 °C) for uncoated and coated samples after pre-heating at 700 °C for 24 h. The electrical conductivity of an oxidized alloy can be expressed as [26, 27]:

$$\frac{1}{\sigma} = \frac{T}{\sigma^* \exp(-E_c/kT)} = \frac{T}{\sigma^*} \exp\left(\frac{E_c}{kT}\right)$$

where σ is electrical conductivity, σ^* is pre-exponent constants, E_c is the activation energy barrier for the conduction process, k is Boltzmann constant, and T is temperature.

E_c can be obtained from the directly proportional relationship between $\ln(\sigma.T)$ and $1/T$ from Eq. (1) [Fig. 5]. Electrical conductivity activation energy of uncoated and coated samples was obtained in order 0.039 eV and 0.03 eV. The lower electrical conductivity activation energy of coated samples caused to the higher electrical conductivity with respect to the uncoated ones and this lower value is because of cobalt spinels in the coated substrates (MnCo_2O_4 , CoCr_2O_4 , CoFe_2O_4 and Co_3O_4).

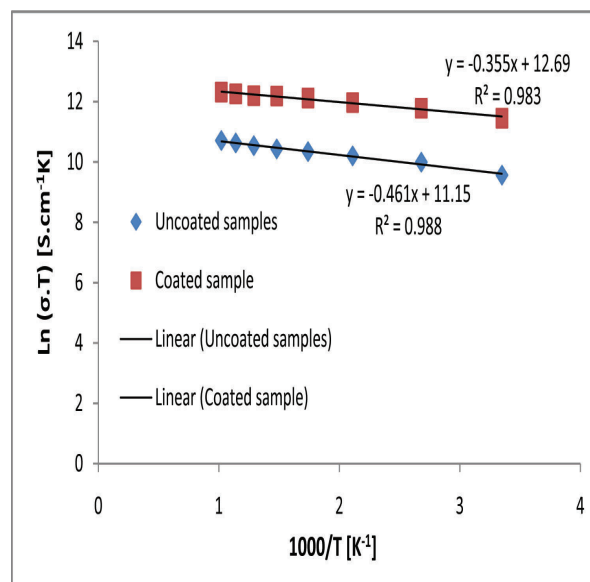


Fig. 5. Electrical conductivity values as a function of temperature for uncoated and coated samples.

4. Conclusion

The formation of $(\text{Mn,Cr})_3\text{O}_4$ spinel, chromia and silica during the oxidation on the surface of bare AISI 430 resulted to the lower values of electrical conductivity because of considerable higher electrical resistance of these phases in comparison with the bare substrate.

The application of spinel compositions (MnCo_2O_4 , CoCr_2O_4 , CoFe_2O_4 and Co_3O_4) increased the high temperature electrical conductivity of AISI 430 ferritic stainless steel used for SOFC interconnects.

The electrical conductivity was obtained 128 S.cm⁻¹ for coated samples and 32 S.cm⁻¹ for uncoated samples after 200 h annealing in static air at 700 ° C.

The electrical conductivity activation energy was obtained 0.039 eV for uncoated samples and 0.03 eV for coated samples.

Acknowledgement

This research has been done by cooperation of Iran New Energies Organization and the authors wish to thank this organization for providing research funding.

References

- [1] W.J. Quadackers, J.P. Abellan, V. Shemet, L. Singheiser, *Materials at High Temperatures*, 20 (2003) 115.
- [2] J.W. Fergus, *Materials Science and Engineering A.*, 397 (2005) 271.
- [3] W.Z. Zhu, S.C. Deevi, *Materials Science and Engineering A.*, 348 (2003) 227.
- [4] H. Ebrahimifar, M. Zandrahimi, *International Journal of Electrical Engineering*, 5 (2010) 2339.
- [5] P. Huczkowski, N. Christiansen, V. Shemet, J.P. Abellan, L. Singheiser and W.J. Quadackers, *Journal of Fuel Cell Science and Technology*, 1 (2004) 30.
- [6] H. Kurokawa, C.P. Jacobson, L.C. DeJonghe, S.J. Visco, *Solid State Ionics*, 178 (2007) 287.
- [7] C. Lee, J. Bae, *Thin Solid Films*, 516 (2008) 6432.
- [8] X. Chen, P.Y. Hou, C.P. Jacobson, S.J. Visco, L.C. De Jonghe, *Solid State Ionics*, 176 (2005) 425.
- [9] Z. Yang, G. Xia, S.P. Simner and J.W. Stevenson., *Journal of the Electrochemical Society.*, 152 (2005) 1896.
- [10] Z. Yang, G. Xia, X. Li and J.W. Stevenson., *International Journal of Hydrogen Energy.*, 32 (2007) 364.
- [11] Z. Yang, G. Xia and J.W. Stevenson., *Electrochemical and Solid-State Letters A.*, 8 (2005) 168.
- [12] W. Wei, W. Chen and D.G. Ivey., *Chemistry of Materials.*, 19 (2007) 2816.
- [13] M.R. Bateni, P. Wei, X. Deng and A. Petric., *Surface & Coating Technology.*, 201 (2007) 4677.
- [14] P. Wei, X. Deng, M.R. Bateni and A. Petric., *Corrosion*, 63 (2007) 529.
- [15] X. Deng, P. Wei, M.R. Bateni and A. Petric., *Journal of Power Sources*, 160 (2006) 1225.
- [16] Y.Sh. Chou, J. W. Stevenson, P. Singh., *Journal of Power Sources.*, 185 (2008) 1001.
- [17] H. Ebrahimifar, M. Zandrahimi, *Int. Journal of Mater. Sci.*, 5 (2010) 465.
- [18] L. Cooper, S. Benhaddad, A. Wood and D.G. Ivey, *J. power sources*, 184 (2008) 220.
- [19] K. Huang, P.Y. Hou and J.B. Goodenough., *Mater. Res. Bull.*, 36 (2001) 81.
- [20] N. Shaigan, D.G. Ivey and W. Chen., *J. Electrochem. Soc.*, 156 (2009) 765.
- [21] H. Ebrahimifar, M. Zandrahimi, *Oxidation of metals*, 75 (2010) 125.
- [22] N. Shaigan, D.G. Ivey and W. Chen., *J. power sources*, Vol. 183 (2008) 651.
- [23] H. Ebrahimifar, M. Zandrahimi, *Solid State Ionics*, 183 (2011) 71.
- [24] H. Ebrahimifar, M. Zandrahimi, *Advanced Materials in Engineering*, 29 (2010) 45.
- [25] N. Shaigan, W. Qu, D.G. Ivey and W. Chen., *J. power sources*, 195 (2010) 1529.
- [26] W.Z. Zhu and S.C. Deevi., *Materials Research Bulletin*, 38 (2003) 957.
- [27] A. Holta and P. Kofstada., *Solid State Ionics.*, 69 (1994) 137.

