Oxidation behavior of Cu-doped MnCo_2O_4 spinel coating on ferritic stainless steels for solid oxide fuel cell interconnects

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Abstract: Spinel oxides with the general formula of $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.1, 0.3, 0.5, 0.7$ respectively) are used as coating materials on the metallic interconnect SUS 430 alloy to reduce the cathodic performance degradation by Cr poisoning and the interfacial resistance to improve the surface stability. The effect of Cu doping at the B position of spinel on the electrical conductivity and coefficient of temperature expansion (CTE) is investigated to determine the oxidation behavior and effectiveness as a protective layer. The result confirms that $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ spinel shows highest

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electrical conductivity of $105.46 \text{ S}\cdot\text{cm}^{-1}$ at 750°C in air and an average CTE value of $12.27\times 10^{-6} \text{ K}^{-1}$ at temperature range of $20\sim 960^\circ\text{C}$. $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coating is stable enough after 2000 h cyclic oxidation at 750°C . The growth of Cr_2O_3 and formation of MnCr_2O_4 in the scale layer are effectively suppressed by the presence of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coating. The oxidation kinetics obeys the parabolic law with a rate constant as low as $2.76\times 10^{-15} \text{ g}^2\cdot\text{cm}^{-4}\cdot\text{s}^{-1}$ and the ASR contributed by the oxide scale is $8.04 \text{ m}\Omega\cdot\text{cm}^2$ at 750°C . The research indicates that $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ is a promising coating material for metallic interconnects of the intermediate temperature solid oxide fuel cells.

Keyword: Solid oxide fuel cell; Alloy interconnect; Copper doped manganese cobaltite spinel; Long-term oxidation; Area specific resistance

1. Introduction

Solid oxide fuel cells (SOFCs) are solid-state devices that generate electricity through an electrochemical reaction between fuel and oxidant at high temperatures, and promising candidates for future energy conversion due to their efficiency in generating electricity from a variety of fuels, such as hydrogen or hydrocarbon fuels [1]. Multiple cells are generally connected in electrical series to increase the output voltage of the SOFC system. The interconnect provides electrical connection between cells and separates fuel and oxidant gases onto the electrodes, which is a key component in a stack of planar solid oxide fuel cells [2]. One of the main challenges in improving the performance and cost-effectiveness of SOFCs is the development of suitable interconnect material. Typical materials used as interconnects include perovskite type ceramic materials based on doped LaCrO_3 for high operation temperatures (900-1000°C) [3] and metallic materials for the IT-SOFC (600-800°C) [2, 4]. Metallic interconnects have potential advantages of high electrical/thermal conductivity, good workability and structural integrity as well as significantly low material cost in comparison to ceramic interconnects, which will totally replace ceramic interconnect for IT-SOFC application [4, 5].

Among the oxidation resistant alloys, Cr_2O_3 -forming ferritic stainless steels, such as SUS 430 and Crofer22 [6, 7], are favored as the candidate materials for the interconnects, which have similar coefficient of temperature expansion (CTE) to other SOFCs components and show quite good electrical conductivity and high workability. These alloys can form well-adhered and dense inner scale of Cr_2O_3 and a less dense outer scale of $(\text{Cr}, \text{Mn})_3\text{O}_4$ spinel, which will reduce Cr vaporization in the form of volatile Cr-containing species [8, 9].

However, for satisfactory long-term performance of SOFCs, the Fe-Cr ferritic stainless steels have to overcome some key issues, which mainly include the unaccepted cathode Cr-poisoning from the chromia-scale evaporation [10, 11] and the increasing electrical resistance due to the scale growth on the metallic interconnects surface and potential spallation [12]. A possible solution to above-mentioned problems can be achieved by modifying the surface of metallic interconnect with an oxide protective coating [13]. Such coatings are required to be dense, electrically conductive, non-volatile and chemically compatible with other cell components [14]. Recently, $(\text{Mn}, \text{Co})_3\text{O}_4$ spinel was reported by researchers to have excellent performance. Excepting for high conductivity and compatible CTE with metallic interconnect,

Yang et al. [13] fabricated $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ coatings onto Crofer22 APU and the effectiveness of the spinel protective layers as a chromium-diffusing barrier was confirmed by a half-year long term test.

To control the sintering, electrical and thermal expansion characteristics of the spinel, a wide range of transition metal cations were used to be doped in spinel structure. The addition of Cu into MnCo_2O_4 spinel can alter the CTE of MnCo_2O_4 spinel and reduce the sintering temperature [15, 16]. Xiao et al. reported $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ spinel with a relatively low ASR after oxidized in air at 750°C for 1000 h [17]. Yang et al. found Ce-modified $(\text{Mn}, \text{Co})_3\text{O}_4$ spinel coating exhibiting a better structural stability and electrical performance compared to samples with the unmodified spinel coating [18].

In this paper, different amount of Cu was doped into the nominal composition of $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.1, 0.3, 0.5$, and 0.7), in order to optimize the properties of MnCo_2O_4 spinel. Then the optimized $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ spinel powders were selected as the coating material on SUS 430 stainless substrate. The properties of the SUS 430 stainless steel with the Cu doped MnCo_2O_4 spinel coating were investigated and compared to the properties of uncoated or MnCo_2O_4 spinel coated SUS 430 stainless steel.

2. Experimental

$\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.1, 0.3, 0.5, \text{ and } 0.7$) and MnCo_2O_4 spinel powders were synthesized via citric acid nitrate process. The desired amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2$ were dissolved in a mixture of distilled water and ethylene glycol (EG, 99.8%, Aladdin). Citric acid (99.8%, Aladdin) was added to the solution under stirring. The mole ratios of the nitrates to citric acid and of the nitrates to EG were maintained at 1:1.2 and 1:1.5, respectively. The mixed solution was heated while stirring, until a gel state was formed. Then, the gel was dried in an oven to reach the combustion point, forming the precursor ash. The ash was calcined in air at 750°C for 3 h.

The prepared powders were subsequently die-pressed into bars under a pressure of 8 MPa and sintered in air at 950°C for 20 h with a relative density of above 95%. The spinel bar with a dimension of 21.50 mm x 5.60 mm x 4.50 mm was used for thermal expansion measurements and electrical conductivity. The thermal expansion behavior was measured by a NETZSCH DIL 402C instrument. The electrical conductivity of the $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.1, 0.3, 0.5, 0.7$ respectively) spinel bars was investigated by the four-probe DC method.

SUS 430 ferritic stainless steel, with chemical composition of

16.76 wt% Cr, 0.69 wt% Mn, 0.75 wt% Si and 0.12 wt% C, was used as the metallic interconnect substrate. A SUS 430 substrate (thickness =1 mm) was cut into a sample with a dimension of 25 mm × 25 mm, then mechanically polished with SiC papers up to 600-mesh and ultrasonically cleaned with ethyl alcohol prior to coating. Coating slurry was prepared by mixing the spinel powders with isopropanol alcohol and binding agent (PVB) and then dip-coated onto the SUS 430 sample. The coated samples were heat-treated in a reducing atmosphere of 5% H₂ +95% N₂ at 800°C for 2 h, then in air at 750°C for another 2 h to prevent significant oxidation of the substrate alloy during coating formation and enhance the densification of spinel coatings at lower temperature [6, 19]. The preparation of MnCo₂O₄ coated SUS 430 alloy sample was through the similar method.

In order to investigate the oxidation behavior of MnCu_{0.5}Co_{1.5}O₄ spinel coated sample, cyclic oxidation tests in oxidation environment was performed in simulating the cathode (air) condition in SOFC. In a test cycle, the sample was heated to 750°C at 5 °C·min⁻¹, held for 50-100 h and then cooled to room temperature. This procedure was repeated 22 times (22 thermal cycles) for an accumulated oxidation time of 2000 h. The weight gain with oxidation time was obtained by weighing different

samples after each thermal cycle using a Sartorius BS-25S electronic balance (accuracy of 0.01 mg). Area specific resistance (ASR) of the oxidized samples was measured using the conventional four-probe DC technique, at temperatures range of 500-800°C in air. Furthermore, to compare the oxidation behavior of $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ and MnCo_2O_4 coated SUS 430 alloy with an electrical current applied, the sample was placed between two Pt meshes, as described in detail in Ref.[20], which was held at 750°C for 200 h in a tubular furnace with an air flowing rate of 100 $\text{mL}\cdot\text{min}^{-1}$, and the applied current density was $0.5\text{ A}\cdot\text{cm}^{-2}$, schematically illustrated in Fig. 1.

To identify the crystal structures and phases of the powders, coating and oxide scale, a PANalytical X'Pert PRO X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation was used. Microstructural and compositional characterizations were performed using a scanning electron microscope (SEM, model Quanta 200) equipped with an energy-dispersive X-ray spectroscopy (EDX) instrument.

3. Results and discussion

Fig.2 shows the powder XRD patterns for $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.1, 0.3, 0.5$, and 0.7) synthesized by the sol-gel method, in comparison with the JCPDS files for MnCo_2O_4 (JCPDS 23-1237)

and CuO (JCPDS 89-5895). Excepting $\text{MnCu}_{0.7}\text{Co}_{1.3}\text{O}_4$, all of the diffraction peaks can be indexed to the cubic spinel phase, assigned to MnCo_2O_4 , which means that reasonable ratio of Cu doping into MnCo_2O_4 causes no significant changes in the crystal structure. Meanwhile, it can be found that with the doping amount of Cu increasing, there is a slight right shift of the diffraction peaks due to the replacement of Co ions with Cu ions, since the radii of Cu^{2+} and Co^{2+} are 0.073 nm and 0.074 nm [21]. Furthermore, with the doping amount of Cu reaches 0.7, the diffraction peaks of CuO can be detected because of the limited solid solubility of Cu in MnCo_2O_4 spinel.

The temperature dependence of the electrical conductivity (σ) for $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.1, 0.3, 0.5$, and 0.7) in air is shown in Fig. 3. The σ value rises with the increasing temperature linearly between $\log(\sigma T)$ and $1/T$, which is consistent with the semiconductor behavior reported for other spinel oxides [22]. This suggests that electrical conduction occurs via small polaron hopping [23]:

$$\sigma = AT \exp(-E_a/kT)$$

(1)

where A is the proportional factor, T the absolute temperature, k the Boltzmann constant, and E_a represents the activation energy for conduction, which are 0.25 eV, 0.23 eV, 0.20 eV and 0.18 eV for

MnCu_xCo_{2-x}O₄ spinel with x=0.1, 0.3, 0.5, and 0.7 respectively. Meanwhile, Ea of MnCo₂O₄ spinel is 0.44 eV in the Ref.[24]. With the doping amount of Cu, the σ value increases before decreasing, and the MnCu_{0.5}Co_{1.5}O₄ spinel has the largest electrical conductivity of 105.46 S·cm⁻¹ at 750°C in air, which is higher than the undoped MnCo₂O₄ spinel of 60 S·cm⁻¹ at 800°C in air[17]. It is known that the electrical conduction in MnCo₂O₄-based spinel proceeds by a hopping mechanism in exchange pairs of Mn³⁺/Mn⁴⁺ on octahedral sites. The incorporation of Cu into MnCo₂O₄ not only leads to the formation of cations with different valence states (e.g., Cu⁺ and Cu²⁺) on octahedral sites, but also induces the transitions of Mn²⁺ and Mn³⁺ to Mn³⁺ and Mn⁴⁺ due to the constraint of charge neutrality. Thus, the presence of cations with different valence states on octahedral sites would facilitate electrical conduction [22]. Furthermore, the limited solid solubility of Cu in MnCo₂O₄ and two-phase coexistence lead to the lower electrical conductivity of MnCu_{0.7}Co_{1.3}O₄ than that of MnCu_{0.5}Co_{1.5}O₄ spinel.

Fig. 4 illustrates the thermal expansion behaviors of the MnCu_xCo_{2-x}O₄ (x=0.1, 0.3, 0.5, and 0.7) spinel. The average CTEs from room temperature (RT) up to 960°C for MnCu_xCo_{2-x}O₄ spinel with x=0.1, 0.3, 0.5, and 0.7 are divided into three stages, which are shown in table. 1. Meanwhile, the CTE of bare SUS 430 alloy is

$12.44 \times 10^{-6} \text{ K}^{-1}$ from room temperature to 850°C , which is in agreement with the Ref. [25]. Obviously, the CTE of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ spinel is more compatible with SUS 430 substrate compared to other Cu doped MnCo_2O_4 spinel. Based on the above research, the electrical conductivity and CTE of the $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ spinel are adequate for it to be used as an alternative spinel protection coating for SOFC metallic interconnects, which will be used as the coating for the further study of long-term oxidation performance on the SUS 430 substrate.

Fig. 5 shows the XRD patterns of the as-coated SUS 430 samples cyclically oxidized at 750°C in air for up to 2000 h. In addition to the weak diffraction peaks generated from the substrate, the primary phase in the oxidized scale is $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ in the all samples. In the period of oxidation at 750°C in air up to 2000 h, the thickness of the oxide scale may increase with time, but the type of phases in the scale remain similar to those prior to the long-term oxidation, which indicates that $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ has a long-term chemical stability. Meanwhile, the diffraction peaks of Cr_2O_3 cannot be found as the coating is relatively thick. It is found by closely comparing the diffraction patterns and the standard JCPDS files, the diffraction peaks of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ phases are slightly left-shifted with the increase of the oxidation time, suggesting the

possible Fe or Mn doping from the substrate[17].

Fig. 6 demonstrates the weight gain of the cyclic oxidation at 750°C in air as a function of oxidation time of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy, along with that of the uncoated for comparison. During the oxidation test, the squared weight gain of the sample increases linearly with time. As reported previously [12, 26], the bare SUS 430 alloy exhibited two-stage oxidation kinetics, represented by K_{P1} and K_{P2} , and the corresponding value for each stage are $1.13 \times 10^{-14} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$ and $1.72 \times 10^{-14} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$, respectively. The first stage oxidation has a lower parabolic rate constant K_{P1} than that of the second state oxidation K_{P2} . Two-stage oxidation was reported in Fe-Cr-Mn alloys [12, 27], which was explained by the formation of M_3O_4 type oxide preceded by the growth of M_2O_3 type oxide. While $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy only exhibits one oxidation behavior, and the corresponding oxidation rate constant K_p is $2.76 \times 10^{-15} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$. Compared with the previous study[17], the rate constant K_p has a slow growth during the increase of oxidation time, but the rate constant of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy is significantly one order of magnitude lower than that of bare SUS 430, indicating that the oxidation rate of the alloy substrate is remarkably reduced by the protective coating $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ spinel, which is consistent with

previous work.

Fig. 7 shows the surface morphologies of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy oxidized at 750°C in air for 0 h (a), 400 h (b), 1500 h (c), and 2000 h (d), respectively. Before the long-term oxidation, the top surface of the coating is consisted of fine oxide grain with a considerable amount of small inhomogeneous pores (Fig. 6a), which may result from the slurry dip-coating process. With the increase of oxidation time, it can be seen that the $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coatings almost has a constant granular size and densification. Especially in Fig. 6d, the $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coating after 22 thermal cycles between room temperature to 750°C (totally holding at 750°C for 2000 h) consists of homogeneous and fine particles with an average size of approximately 0.5-1 μm . The coating is stable, crack free, with good adhesion to the substrate.

To determine the microstructure and element distribution among the oxide layer, EDS line scan analysis is performed on the cross-section of the $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy oxidized at 750°C in air for 0 h and 2000 h (Fig. 8). Before the long-term oxidation, the cross-section of the coating with a thickness of 6-7 μm (Fig. 8a) shows a relatively dense and continuous interface between the protecting coating and substrate. While after 2000 h oxidation, the coating layer (Fig. 8c) is homogeneous and dense in

the inner region but relatively loose in the outer region, with total thickness of approximately 11-12 μm , which is much thicker than that before oxidation. However, both of the coating layers confirm that the spinel layer exhibits excellent adhesion with the SUS 430 substrate, which would be expected to be able to act as a barrier for the outward diffusion of cations and inward diffusion of oxygen ions. Although there are a relatively similar elements distribution between the as-coated sample (0 h) and the oxidized sample (2000 h), the EDS analysis (Fig. 8b and Fig. 8d) of the coating layers indicates that two distinct layers existing in the as-coated sample and three distinct layers existing in the oxidized sample. Excepting the oxidized layer and the coating layer, a rather obvious interfacial region is formed in the oxidized sample. The interfacial region contains Cr, Mn, Co and Cu, which could be the result of a solid-state reaction and/or diffusion between the oxidized layer and the coating layer. Combined with the XRD result, the phase in the coating layer is still spinel $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ and no obvious Cr can be detected cross the coating layer. This result confirms that the Cr-rich oxide is covered by the $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ spinel and no Cr-containing species is exposed directly to air. Compared to the oxide scale thermally grown on the uncoated SUS 430 alloy, Cr_2O_3 flakes and MnCr_2O_4 spinel grains are presented to form oxide scale,

as shown in Ref. [6], which is impossible to avoid the chromia-scale evaporation and potential cathode poisoning in SOFC cathode atmosphere.

The area specific resistance (ASR, $\text{m}\Omega\cdot\text{cm}^2$) is another property of metallic interconnects, reflecting both the conductivity and the thickness of the oxide scale, which is significantly important for the overall performance of SOFCs and conventionally adopted as a measurement of the electrical performance of the interconnect. Fig. 9 displays the Arrhenius plots of ASR of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy as a function of measurement temperature in air after cyclically oxidized at 750°C in air for 2000 h. The detail calculation of the ASR can be found in Ref. [28]. $\log(\text{ASR}/T)$ is linearly proportional to $1/T$, showing the electrical behavior of semi-conductors. For the $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy oxidized at 750°C for 2000 h, the ASR of the sample is $8.04 \text{ m}\Omega\cdot\text{cm}^2$ at 750°C in air, which is about one order of magnitude lower than that of the uncoated SUS 430 alloy [12], similar to that of MnCo_2O_4 coated SUS 430 alloy oxidized at 750°C in air for 850 h [29] and NiMn_2O_4 coated SUS 430 alloy oxidized at 750°C in air for 1000 h [30]. The corresponding ohmic loss associated with the ASR at conventional current density $0.5 \text{ A}\cdot\text{cm}^{-2}$ is only 4.02 mV. Such a low ASR is attributed to the high conductivity of

MnCu_{0.5}Co_{1.5}O₄ compared with that of Cr₂O₃ or MnCr₂O₄.

Applied electrical current is one of the important factors influencing high temperature oxidation of SOFC interconnects. Li et al. [31] found a thicker oxide scale on the negative side when the Crofer 22 APU oxidized in coal syngas at 800°C with an electrical current applied. This phenomenon was a result of the influence of applied current, which enhanced outward diffusion of metal ions from the alloy substrate to the scale/gas interface. Fig. 10 shows the ASR tendencies of MnCu_{0.5}Co_{1.5}O₄ and MnCo₂O₄ coated SUS 430 alloy as a function of time at 750°C in air for 200 h with current density of 0.5 A·cm⁻². The MnCo₂O₄ coated SUS 430 alloy demonstrates an initial electrical resistance of 7.2 mΩ·cm² and then it increases steadily to about 7.7 mΩ·cm² after 200 h. However, for the sample with MnCu_{0.5}Co_{1.5}O₄ coating, it starts with a low ASR of 6.6 mΩ·cm² and then decreases to less than 6.4 mΩ·cm² in the first few hours; although the ASR also increases slowly with time, however it only reaches to about 6.5-6.6 mΩ·cm² after 200 h measurement. The result reveals that Cu doped MnCo₂O₄ spinel coating also has a better electrical performance even under applied current.

4. Conclusions

Cu doped MnCo₂O₄ spinel powders are prepared via citric

acid-nitrate method. $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ spinel shows high electrical conductivity and excellent thermal expansion compatibility with the SUS 430 alloy, with average CTE value of $12.27 \times 10^{-6} \text{ K}^{-1}$ from room temperature up to 960°C and the conductivity of $105.46 \text{ S}\cdot\text{cm}^{-1}$ at 750°C . The $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coating can significantly increase the oxidation of SUS 430 alloy, and the kinetics of cyclic oxidation obey the parabolic law with a rate constant K_p of $2.76 \times 10^{-15} \text{ g}^2\cdot\text{cm}^{-4}\cdot\text{s}^{-1}$. After cyclically oxidized at 750°C for 22 cycles with total time of 2000 h, the ASR of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy is only $8.04 \text{ m}\Omega\cdot\text{cm}^2$. The $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy also exhibits a low and stable ASR with an applied current density of $0.5 \text{ A}\cdot\text{cm}^{-2}$ at 750°C for 200 h. The results demonstrate that the Cu-doped MnCo_2O_4 coating is an excellent coating material for metallic interconnects of the intermediate temperature SOFCs.

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Table.1 The CTE data of the $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.1, 0.3, 0.5, 0.7$ respectively) spinel from room temperature to 960°C.

	K₁(RT-180°C)	K₂(RT-280°C)	K₃(RT-960°C)
MnCu_{0.1}Co_{1.9}O₄	24.90x10 ⁻⁶ K ⁻¹	15.40x10 ⁻⁶ K ⁻¹	11.58x10 ⁻⁶ K ⁻¹
MnCu_{0.3}Co_{1.7}O₄	21.20x10 ⁻⁶ K ⁻¹	12.60x10 ⁻⁶ K ⁻¹	11.65x10 ⁻⁶ K ⁻¹
MnCu_{0.5}Co_{1.5}O₄	22.30x10 ⁻⁶ K ⁻¹	13.70x10 ⁻⁶ K ⁻¹	12.27x10 ⁻⁶ K ⁻¹
MnCu_{0.7}Co_{1.3}O₄	22.00x10 ⁻⁶ K ⁻¹	13.30x10 ⁻⁶ K ⁻¹	11.21x10 ⁻⁶ K ⁻¹
SUS 430	12.44x10 ⁻⁶ K ⁻¹ (RT-850°C)		

Figure captions

Fig. 1 Schematic diagram of ASR measurement setup.

Fig.2 X-ray patterns of $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.1, 0.3, 0.5, 0.7$ respectively).

Fig. 3 Temperature dependence of electrical conductivity for the $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.1, 0.3, 0.5, 0.7$ respectively) spinel in air from 500 to 800°C.

Fig. 4 Thermal expansion behaviors of the $\text{MnCu}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.1, 0.3, 0.5, 0.7$ respectively) spinel.

Fig.5 XRD patterns of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy oxidized at 750°C in air for up to 2000h.

Fig. 6 Squared oxidation weight gain of bare and $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy as a function of oxidation time at 750°C in air.

Fig. 7 Surface morphologies of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy oxidized at 750°C in air for 0 h (a), 400 h (b), 1500 h (c), and 2000 h (d).

Fig. 8 The cross sectional (a, c) morphologies and EDS compositional profile (b, d) of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy oxidized at 750°C in air for 0 h (a, b) and 2000 h (c, d).

Fig. 9 Dependence of ASR of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ coated SUS 430 alloy as a function of measurement temperature in air after

cyclically oxidized at 750°C in air for 2000h.

Fig. 10 Interfacial ASR of $\text{MnCu}_{0.5}\text{Co}_{1.5}\text{O}_4$ and MnCo_2O_4 coated SUS 430 alloy at 750°C for 200 h with a constant current density of $0.5\text{A}\cdot\text{cm}^{-2}$.

Fig. 1

Fig. 2

Fig.3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10