International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:9, No:7, 2015

Synthesizing $CuFe_2O_4$ Spinel Powders by a Combustion-Like Process for Solid Oxide Fuel Cell Interconnect Coatings

S. N. Hosseini, M. H. Enayati, F. Karimzadeh, N. M. Sammes

***Abstract*—**The synthesis of $CuFe_2O_4$ spinel powders by an optimized combustion-like process followed by calcination is described herein. The samples were characterized using X-ray diffraction (XRD), differential thermal analysis (TG/DTA), scanning electron microscopy (SEM), dilatometry and 4-probe DC methods. Different glycine to nitrate (G/N) ratios of 1 (fuel-deficient), 1.48 (stoichiometric) and 2 (fuel-rich) were employed. Calcining the as-prepared powders at 800 and 1000℃ for 5 hours showed that the G/N ratio of 2 results in the formation of the desired copper spinel single phase at both calcination temperatures. For G/N=1, formation of $CuFe_2O_4$ takes place in three steps. First, iron and copper nitrates decompose to iron oxide and pure copper. Then, copper transforms to copper oxide and finally, copper and iron oxides react with each other to form a copper ferrite spinel phase. The electrical conductivity and the coefficient of thermal expansion of the sintered pelletized samples were 2 $S.cm^{-1}$ (800°C) and 11×10^{-6} $°C^{-1}$ (25-800°C), respectively.

***Keywords*—**SOFC interconnect coatings, Copper ferrite, Spinels, Electrical conductivity, Glycine–nitrate process.

I. Introduction

FERRITIC stainless steel alloys have attracted attention for use as solid oxide fuel cell (SOFC) interconnects. One of the most effective approaches to improve the ferritic stainless steel interconnect performance is to apply a surface coating to enhance conductivity and reduce oxide scale growth and Cr volatility.

Spinels can serve as barriers to Cr cation migration and possess high electronic conductivity [1], [2]. Cubic spinels have the general formula of AB_2O_4 with A and B being divalent, trivalent and quadrivalent cations in octahedral and tetrahedral sites, and oxygen anions on the face centered cubic (FCC) lattice sites. Depending on the choice of A and B cations and their ratio, spinels can be good electronic conductors and show excellent coefficient of thermal expansion (CTE) match with the ferritic stainless substrate and other cell components. Spinel coatings have shown excellent capability for absorbing Cr species that migrate from the chromia-rich scale to the scale surface and cause Cr poisoning.

Research studies have been conducted to evaluate the suitability of different spinel compositions for application as potential conductive/protective coatings for stainless steel interconnects. It has been found that spinels containing Fe exhibited the closest CTE values to ferritic stainless steels [3], [4].

In the present study, the copper ferrite spinel was considered as one suitable candidate for the purpose of interconnects coating. The aim of this paper was to synthesis $CuFe_2O_4$ spinel powder using the GNP method, and to investigate its capability as an interconnect coating. Further, the CTE and electrical conductivity of the samples are examined.

II. Experimental

A. Materials Preparation

In order to prepare Cu-Fe-O spinel (nominal $CuFe_2O_4$) the proportional amounts of copper (II) nitrate tri-hydrate ($Cu(NO_3)_2.3H_2O$, Sigma Aldrich, 99%) and iron (III) nitrate nona-hydrate ($Fe(NO_3)_3.9H_2O$, Sigma Aldrich, 99%) were dissolved in 200 ml distilled water. After complete dissolution, glycine (NH_2CH_2COOH, Sigma Aldrich, 99%) was added according to three G/N ratios of 1 (fuel-deficient), 1.48 (stoichiometric) and 2 (fuel-rich). The solution was continuously stirred at room temperature and after 15 min the temperature of the heating plate was raised to approximately 120°C. After approximately 2 h stirring, the solution turned to a highly viscous black–brown gel. By increasing the temperature, an auto ignition reaction spontaneously occurred in the precursor, upon which a large amount of gaseous phase was released. The resulting powder was calcined in static air at two different temperatures of 800°C and 1000°C for 2 h (heating and cooling rate of 5°C.min^{-1}). To investigate conductivity and thermal expansion coefficient of the resulting $CuFe_2O_4$ powder, the sample was uni-axially pressed into pellets. The obtained cold pressed pellets were subsequently sintered at 950°C for 2 h with a heating and cooling rate of 10°C.min^{-1}. The relative density of the pelletized samples was determined using the Archimedes method and was observed to be approximately 70%.

B. Measurement and Characterization

XRD analysis of the samples was performed using room-temperature X-ray diffraction (RT-XRD) analysis on an X-ray

S.N. Hosseini was with the Department of Chemical Engineering, Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Gu, Pohang 790–784, Republic of Korea. She is now with Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran (Corresponding author: Tel.: 983113915744; fax: 983113912752; e-mail: n.hosseini@ma.iut.ac.ir).

N.M. Sammes is with the Department of Chemical Engineering, Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Gu, Pohang 790–784, Republic of Korea.

M.H Enayati and F. Karimzadeh are with the Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran.

analyzer (D/max 2500PC, Rigaku) (Ni-filtered Cu Kα radiation, operated at 40 kV, 20 mA). The precursor was collected prior to combustion reaction for thermal analysis measurement. The TG/DTA profiles were recorded by a thermal analyzer (Labsyse-Calisto) within the temperature range of 30–850°C in flowing air (30 ml/min) with heating rate of 10 °C/min. CTE measurements were performed using a NETZSCH DIL 402PC dilatometer from room temperature to 850°C in air. The electrical conductivity was measured using the standard DC four-point technique from 500 to 800°C in air.

III. Results and Discussion

We selected glycine (NH_2CH_2COOH) because it serves two principal purposes [5], [6]:

- Firstly, it is known to act as a complexing agent for a number of metal ions containing a carboxylic acid group at one end and an amino group at the other end. In solution, glycine becomes a zwitterion and it can effectively complex metal ions of varying ionic sizes to form polynuclear coordination compounds;
- Secondly, it is a very good "fuel" for the combustion reaction, being oxidized by nitrate ions.

GNP produces N_2, H_2O and CO_2 as the gaseous products [5], [6]. When the combustion is complete, the reaction equation can be expressed as:

$$18\ Fe(NO_3)_3 + 9\ Cu(NO_3)_2 + 40\ NH_2CH_2COOH \rightarrow 9\ CuFe_2O_4 + 100\ H_2O + 56\ N_2 + 80\ CO_2 \quad (1)$$

The initial composition of the mixture containing metal nitrates and glycine was derived from the total oxidizing and reducing valences of the oxidizer and fuel via propellant chemistry [5], [6]. The stoichiometric composition of the redox mixture needed is 2(−15)+1(−10)+ n(+9)=0, or n=40/9. Hence, the stoichiometric G/N ratio will be (40/9)/3=1.48.

By adjusting the G/N molar ratio, we can control the flame temperature and the nature of the combustion reaction [7]. Thus, to obtain a proper G/N ratio that corresponds to a complete combustion with a desired spinel product, we studied the behavior of three systems with G/N molar ratios of 1 (fuel-deficient), 1.48 (stoichiometric) and 2 (fuel-rich).

The XRD patterns of the precursors with different G/N molar ratios, prepared by the combustion reaction process, after calcination at different temperatures are shown in Fig. 1.

For both G/N ratios of 1 and 1.48, although the main component is copper ferrite phase it also contains some CuO and Fe_2O_3 phases after calcination at 800°C (Fig. 1 (a)). The Fe_2O_3 peaks disappear after heating at 1000°C (Fig. 1 (b)), but some diffraction peaks belonging to CuO are still present in these samples. However, in the case of G/N ratio of 2, $CuFe_2O_4$ is the only phase produced after calcination at 800 and 1000°C, indicating that this molar ratio is suitable to synthesize a single copper ferrite phase. Since complete combustion occurred at this ratio, resulting in the formation of desired spinel phase, all other experiments were performed using this ratio.

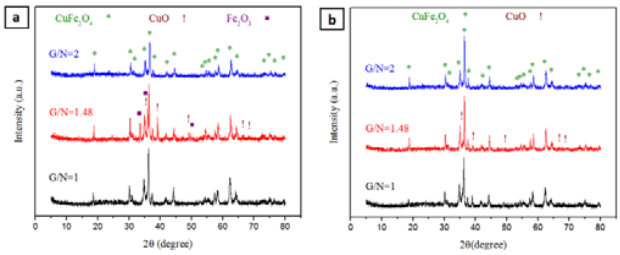

Fig. 1 The XRD patterns of the combustion synthesized products from the precursors with different amounts of G/N ratios after calcinations for 5 h at (a) 800 and (b) 1000°C

Simultaneous TG/DTA investigations in air (heating rate of 10°C/min) were carried out on precursors with G/N=2 to study its combustion behavior. As shown in Fig. 2, there is one endothermic and two exothermic peaks on the DTA trace. A small weight loss of about 11% up to 130°C can be observed, which is associated with a weak endothermic signal. This can be attributed to the dehydration reaction of the precursor. A strong exothermic event at approximately 157°C, with an onset temperature of 130°C, causes a sudden weight loss of 83.8% in the range of 130-170°C, due to the combustion reaction of the glycine–nitrate precursor. This is followed by a third exothermic peak at 300°C, with a weight loss of 25% taking place in the temperature range of 170-370 °C. As no further weight loss or peak can be seen in the TG/DTA curves, one can conclude that the thermal decomposition of the precursor is completed below 400°C.

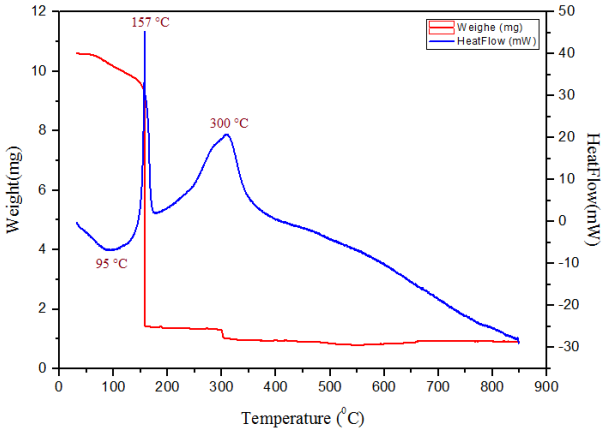

Fig. 2 The simultaneous TG/DTA investigations of the precursor with G/N=2

To investigate the corresponding transformations and reaction mechanisms, the precursor was heated using the DTA up to 200, 400, 600 and 800°C under identical conditions, and then characterized using XRD (Fig. 3).

As can be seen in Fig. 3, after DTA up to 200°C, just Cu and Fe_2O_3 peaks are present in the XRD pattern suggesting that thermal decomposition reactions have finished in the precursor according to following reaction:

$18\ Fe(NO_3)_3.9H_2O + 9\ Cu(NO_3)_2.3H_2O + 54C_2H_5NO_2 + 31.5\ O_2 \rightarrow 9\ Cu + 9\ Fe_2O_3 + 63\ N_2 + 108\ CO_2 + 324\ H_2O$
ΔH^0_{298}=-29786.5 kJ (2)

Thus the first exothermic peak at 157°C on the DTA curve is attributed to this reaction.

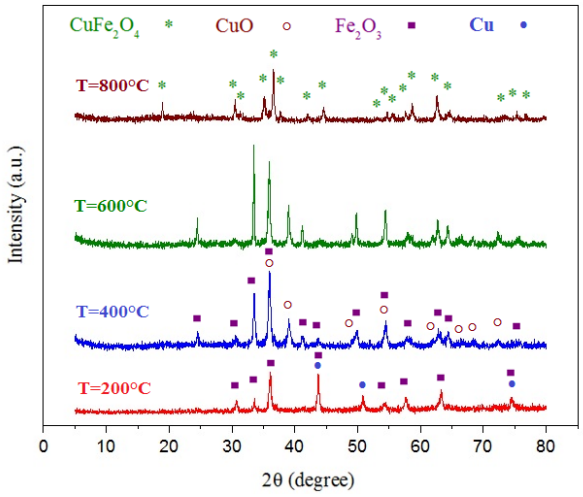

Fig. 3 The XRD patterns of the precursor with G/N=2 after DTA up to different temperatures.

By increasing the annealing temperature to 400°C, Cu peaks disappear in the XRD pattern (Fig. 3) and CuO peaks are observed. Therefore, the exothermic peak located at a temperature of approximately 300°C correspond to copper oxidation to form CuO which can be expressed as:

$Cu+0.5O_2=CuO \quad \Delta H^0_{298}$=-157.3 kJ (3)

No new phase is detected on XRD patterns upon further heating to 600°C. However, by increasing the temperature to 800°C, all XRD peaks are replaced with $CuFe_2O_4$ traces (Fig. 3) confirming that formation of $CuFe_2O_4$ spinel starts above 600°C according to this reaction:

$CuO+Fe_2O_3=CuFe_2O_4 \quad \Delta H^0_{298}$=+22.6 kJ (4)

There are no peaks on the DTA curve in this temperature range corresponding to the above reaction. Thus it may be inferred that the reaction between copper and iron oxides, to form copper ferrite spinel, proceeds gradually over the temperature range of 600-800°C. Another reason for the absence of this endothermic peak on the DTA curve can be the heat of reaction which is much smaller than two other enthalpy changes of reactions (2) and (3). This also implies that the formation of crystalline $CuFe_2O_4$ is driven by diffusion kinetics.

Based on thermal analysis and XRD data, it can be concluded that formation of $CuFe_2O_4$ from the ash containing copper and iron nitrates and glycine with a molar G/N ratio of 2 takes place in three steps. In the first step iron and copper nitrates decompose to Fe_2O_3 and Cu, respectively. In the second step, Cu changes to CuO and finally CuO reacts with Fe_2O_3 to form $CuFe_2O_4$ spinel at higher temperatures.

The SEM analysis of the prepared $CuFe_2O_4$ powder with a molar ratio of 2 shows the formation of foamy agglomerate particles and the presence of large amounts of pores in their sponge-like structure (Fig. 4). Formation of these features is attributed to the evolution of the large amount of gas released during the combustion reaction [7].

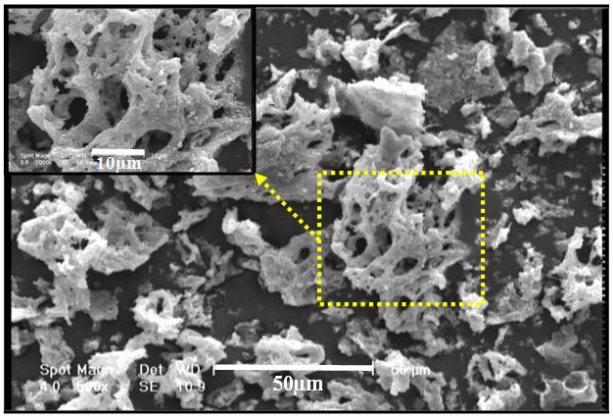

Fig. 4 The SEM image of $CuFe_2O_4$ morphology

To examine whether $CuFe_2O_4$ can be used as a conductive coating material for ferritic stainless steel, the CTE and electrical conductivity of the spinel were measured. Fig. 5 shows the thermal expansion curve, from which the CTE of the sample was calculated. Over the temperature range of 25-800°C, the CTE of $CuFe_2O_4$ is approximately 11×10^{-6} $°C^{-1}$ which is the same value reported for ferritic stainless steel in this range. As mentioned before, it was found that spinels containing Fe exhibited the closest CTE values to ferritic stainless steels (11×10^{-6} $°C^{-1}$) [1]-[3].

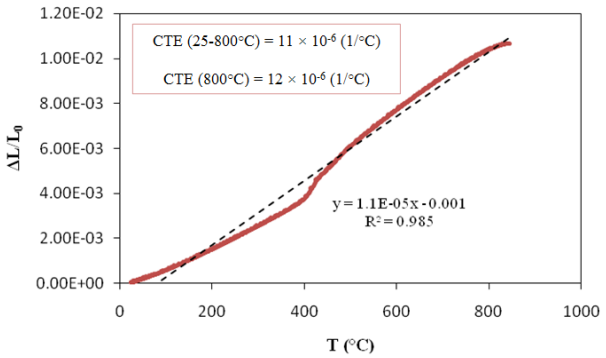

Fig. 5 Thermal expansion of $CuFe_2O_4$ bulk sample measured from room temperature to 800°C

The temperature dependence of the electrical conductivity, for the $CuFe_2O_4$ spinel in air is presented in Fig. 6. As can be seen, the electrical conductivity of the sample increases by increasing the temperature, indicating the thermally activated mobility of charge carriers based on the hopping conduction mechanism. The octahedral cations are responsible for

electrical conduction in the spinels. In fact, hopping motion of charges with thermally activated mobility occurs between octahedral sites [7].

The electrical conductivity of the $CuFe_2O_4$ spinel is 2 $S.cm^{-1}$ at 800°C which is 2 times greater than the well-accepted minimum electrical conductivity for useful interconnects in SOFC's (1 $S.cm^{-1}$) [8]. It should be noted that the relatively poor density of the pelletized sample (approximately 70%), due to the existence of large and porous agglomerates, affects its electrical conductivity [7]. Thus, increasing the sample density is expected to improve the electrical conductivity.

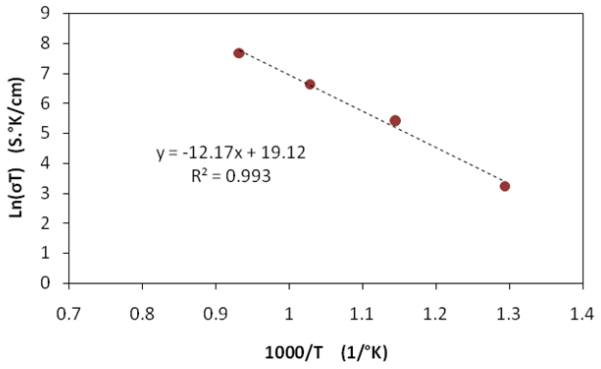

Fig. 6 Arrhenius plot of the electrical conductivity of $CuFe_2O_4$ from 500 to 800°C

In conclusion, both the CTE and the electrical conductivity results reveal that $CuFe_2O_4$ spinel is potentially suitable to be used as an alternative protection coating for SOFC metallic interconnects.

IV. Conclusion

In this research, synthesizing copper ferrite spinel powders by a GNP method with different G/N molar ratios followed by calcination was investigated. The results can be summarized as follows:

- The desired single spinel phase is completely formed in the fuel-rich G/N ratio of 2 at 800 and 1000°C, while CuO and/or Fe_2O_3 phases are also present in these samples for the fuel-lean and stoichiometric ratios of 1 and 1.48, respectively.
- The $CuFe_2O_4$ formation from the ash containing copper and iron nitrates and glycine with a molar G/N=2, occurs in three steps. The first step includes decomposing iron and copper nitrates to Fe_2O_3 and Cu, respectively, while the second step involves oxidation of Cu to CuO. In the final step, CuO reacts with Fe_2O_3 to form $CuFe_2O_4$ spinel at higher temperatures.
- The electrical conductivity of the $CuFe_2O_4$ spinel was observed to be 2 $S.cm^{-1}$ at 800°C which is 2 times greater than the well-accepted minimum electrical conductivity for the use as interconnects in an SOFC.
- The dilatometry measurements revealed that the CTE of $CuFe_2O_4$ is approximately 11×10^{-6} $°C^{-1}$ over the temperature range of 25-800°C, which is very close to the CTE for ferritic stainless steel.
- All results showed that $CuFe_2O_4$ spinel is a good candidate to be used as an alternative protection coating for SOFC metallic interconnects.

References

[1] P. Paknahad, M. Askari, and M. Ghorbanzadeh, "Application of sol-gel technique to synthesis of Copper-Cobalt spinel on the ferritic stainless steel used for solid oxide fuel cell interconnects", *J. Power Sources*, vol. 266, pp. 79, 2014.

[2] S. Joshi, C. Silva, P. Wang, Y. Mozharivskyj, and A. Petric, "Copper-Magnesium-Manganese spinel coatings for solid oxide fuel cell interconnects", *J. Electrochem. Soc.*, vol. 161, pp. F233, 2014.

[3] N. Shaigan, W. Qu, D.G. Ivey, and W. CheN, "A review of recent progress in coatings, surface modifications and alloy developments for solid oxide fuel cell ferritic stainless steel interconnects", *J. Power Sources*, vol. 195, pp. 1529, 2010.

[4] W. Qu, L. Jian, J.M. Hill, and D.G. Ivey, "Electrical and microstructural characterization of spinel phases as potential coatings for SOFC metallic interconnects", *J. Power Sources*, vol. 153, pp. 114, 2006.

[5] D. Gingas¸ I. Mindru, L. Patron, O. Carp, D. Matei, C. Neagoe, and I. Balint, "Copper ferrite obtained by two soft chemistry routes", *J. Alloys Compd.*, vol. 425, pp. 357, 2006.

[6] V. Berbenni, A. Marini, C. Milanese, and G. Bruni, "Solid state synthesis of $CuFe_2O_4$ from $Cu(OH)_2.CuCO_3$– $4FeC_2O_4.2H_2O$ mixtures: mechanism of reaction and thermal characterization of $CuFe_2O_4$", *J. Therm. Anal. Calorim.*, vol. 99, pp. 437, 2010.

[7] N. Hosseini, F. Karimzadeh, M.H. Abbasi, and G.M. Choi, "Microstructural characterization and electrical conductivity of $Cu_xMn_{3-x}O_4$ ($0.9\leq x\leq 1.3$) spinels produced by optimized glycine–nitrate combustion and mechanical milling processes", *Ceram. Int.*, vol. 40, pp. 12219, 2014.

[8] S.C. Singhal, "High temperature solid oxide fuel cells: fundamentals, design and applications", *Elsevier, Ltd.*, 2003.