Journal of Alloys and Compounds 508 (2010) L5–L8

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

Influence of fabrication process of Ni–$BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ cermet on the hydrogen permeation performance

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ARTICLE INFO

Article history:
Received 30 April 2010
Received in revised form 7 August 2010
Accepted 13 August 2010
Available online 20 August 2010

Keywords:
Sintering
Ceramics
Chemical synthesis
X-ray diffraction

ABSTRACT

A dense hydrogen permeable composite membranes consisting of Ni and $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BCZY) were fabricated by a packing method at a lower temperature than the powder-mixing method. The results of backscattered electron microscope (BSEM) and scanning electron microscope (SEM)-energy dispersive analysis system of X-ray (EDS) revealed that the membrane derived from the packing method showed the most uniform mixture of the Ni phase and the BCZY phase. The hydrogen permeation measurement showed that a more uniform microstructure would result in higher hydrogen permeation.

1. Introduction

Technologies for high-purity hydrogen from the reforming and partial oxidation of natural gas using membrane technology have high potential for gas and energy industries [1,2]. A composite membrane consisting of electronic conductor Ni and a solid proton conductor $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ or Lanthanum doped ceria was used for hydrogen separation without the need for electrodes or external electrical circuit, which is more cost-effective than traditional gas separation [3–5]. The Ni–BCZY composite membrane shows good performance and adequate stability in the atmosphere containing H_2O, H_2S and CO_2 [1,2,6–8]. In previous works, the composite membranes are generally prepared by directly mixing the metal Ni and BCZY oxide powders followed by a pressing and sintering process, however, these composite membranes are usually sintered at a high temperature up to 1430 °C [7,8]. Therefore, there is a great interest in developing a facile method to reduce the sintering temperature. Another problem for the simple mechanical mixing method is that the powders are not mixed uniformly. In order to solve these problems, we propose a modified citric acid–nitrate gel combustion method which can provide high active composite powders to reduce the sintering temperature as well as improve the homogeneity of the composite membrane. In this study, dense Ni–BCZY cermets are successfully fabricated after sintering at a low temperature of 1300 °C by using the active powders prepared by the modified citric acid–nitrate gel combustion method. More importantly, the cermet attains a higher performance than the sample prepared by a traditional method.

2. Experimental procedure

The mechanical mixing powders method and the packing method were used to prepare the composite powders of 50 wt.% BCZY–50 wt.% Ni (corresponding to a volume rate of 60:40). Fig. 1 shows the two methods and the abbreviated names of the composites prepared by the two different methods. The detailed information for these two methods can be found in Refs. [9–11]. The BCZY powders were synthesized by citric acid–nitrate gel combustion method with the raw materials of $Ce(NO_3)_3{\cdot}6H_2O$, $Ba(NO_3){\cdot}9H_2O$, $Y(NO_3)_3{\cdot}6H_2O$, and $Zr(NO_3)_4{\cdot}5H_2O$ at proper molar ration and then calcined at 1000 °C for 3 h. Ni–BCZY-1 was prepared by mixing the commercial Ni powders (99.5%) and BCZY powders. The obtained powders were ball-milled in alcohol for 24 h, dried, ground, and then pressed uniaxially with a diameter of 15 mm. This method is extensively used to prepare ceramic–ceramic and ceramic–metal composites, but it is difficult to obtain homogeneous mixture. The composite powders of fabricating the Ni–BCZY-2 composite membrane were prepared as follows. Firstly, $Ni(NO_3)_2{\cdot}6H_2O$ was dissolved in water, then BCZY powders were added into the Ni^{2+} solution under stir. Subsequently, citric acid with molar ratios of soluble metal ions: citric acid of 1:1.5 was added and pH value was adjusted to about 7 with ammonia. The suspension was heated up under continuous stirring until ignition and combustion occurred, getting as-prepared composite powders. Under this condition, the Ni phase was packed by the BCZY phase through this method because the Ni phase is less than the BCZY phase. All the pellets were pressed under 6 MPa for several minutes. The Ni–BCZY-1 pellets were sintered at 1430 °C for 10 h and at 1400 °C for 5 h in 4% H_2 balanced with Ar, and the Ni–BCZY-2 pellets were sintered at 1400 °C, 1350 °C, 1300 °C for 5 h under 4% H_2 balanced with Ar, respectively. Density of the pellets was measured in mercury by an Archimedes method. The hydrogen permeation flux measurement was carried out in a self-built apparatus [5,6]. After polishing to 1 mm, the sintered pellets were sealed on an alumina tube with a glass ring sealant at 990 °C for 30 min. The feed gas was acquired by mixing 20 mL/min high purity H_2 and 80 mL/min N_2 followed by bubbling through

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doi:10.1016/j.jallcom.2010.08.040

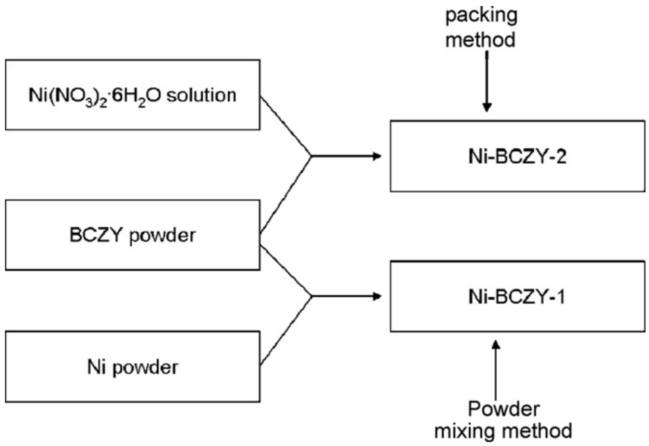

Fig. 1. Scheme of preparing the composite powders.

deionized water at 25 °C. The sweep gas was high purity Ar (99.99%) with a flow rate of about 20 mL/min. The permeated effluent gas was analyzed with on-line gas chromatography. The hydrogen leakage rates were below 5% during our measurement. The phase composition for as-prepared powders and membrane materials was analyzed by XRD (Philips X'Pert Pro Super, Cu Kα, 40 kV, 50 mA). The microstructure and phase composition of the samples was observed by a SEM (JEOL JSM-6390LA) equipped with an EDS system.

3. Results and discussion

Fig. 2 shows the XRD patterns of the composite membrane disks as well as the BCZY powders and the composite powders. The XRD pattern of BCZY is shown in Fig. 2a, we can see that the pure perovskite structure is formed. The XRD pattern of composite powders prepared by the packing method is shown in Fig. 2b. It can be seen that the basic phases are BCZY and NiO, but some other phases such as $BaCO_3$ and Y doped CeO_2–ZrO_2 solutions could also be found, which is ascribed to the reaction between BCZY and CO_2 generating from the combustion of organic matters according to Eq. (1) [12,13]

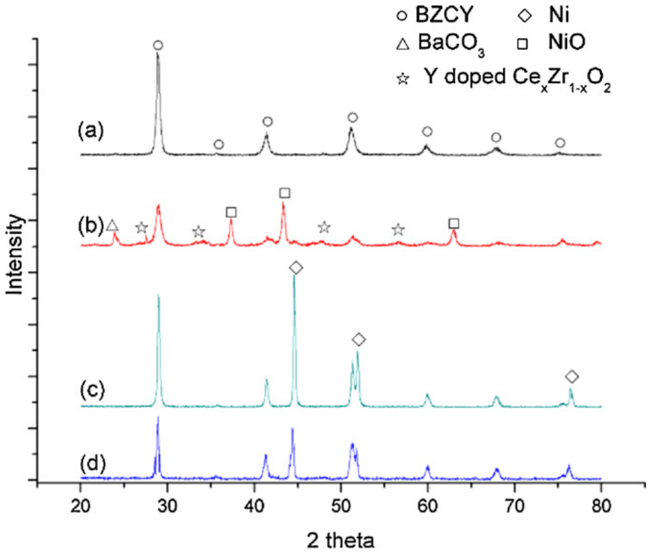

Fig. 2. XRD patterns for (a) BCZY, (b) composite BCZY/NiO and (c) Ni–BCZY-1, (d) Ni–BCZY-2.

$$BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{2.9} + CO_2 \rightarrow BaCO_3 + Ce_{0.7}Zr_{0.1}Y_{0.2}O_{1.9} \tag{1}$$

Fig. 2c and d are the XRD patterns obtained from the surfaces of Ni–BCZY cermets prepared by the above two different methods. From the patterns, only peaks corresponding to Ni and BCZY appear. It means that NiO would be reduced at proper temperatures for

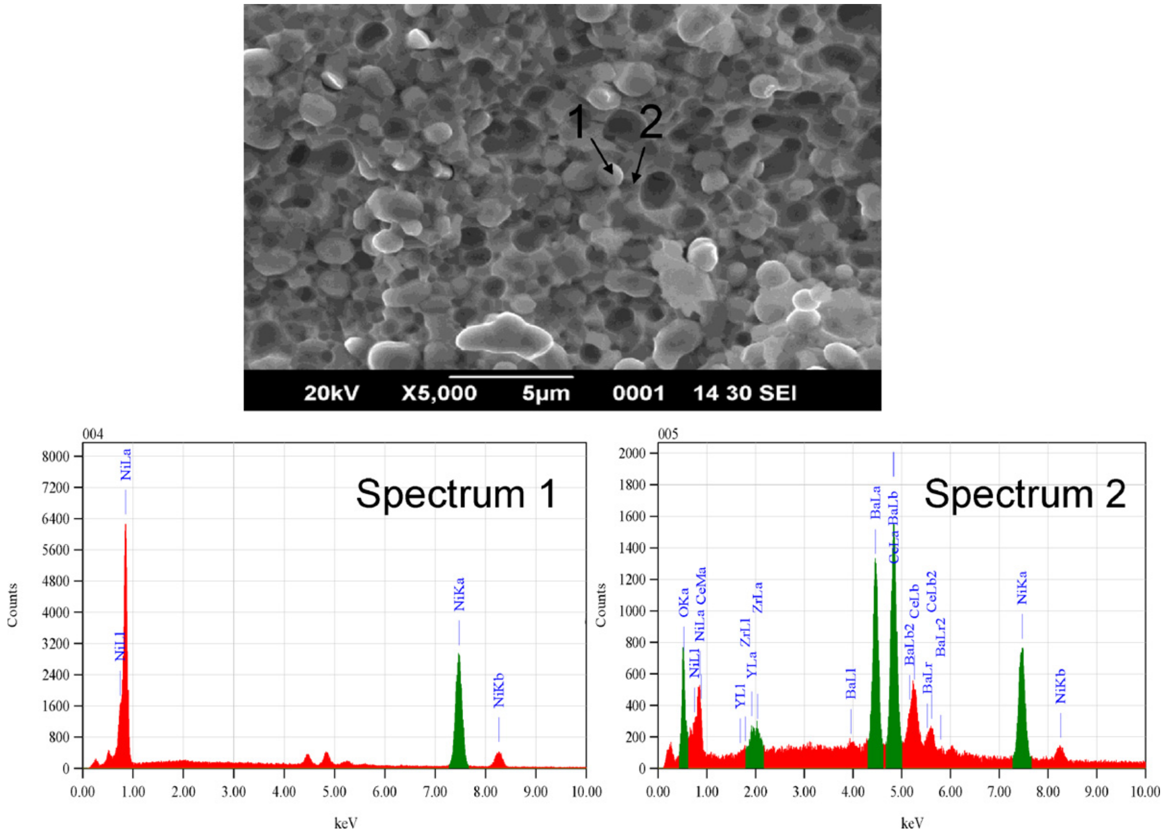

Fig. 3. SEM-EDS analysis of the cermet of Ni-BCZY-2: (1) conglobation and (2) around of conglobation.

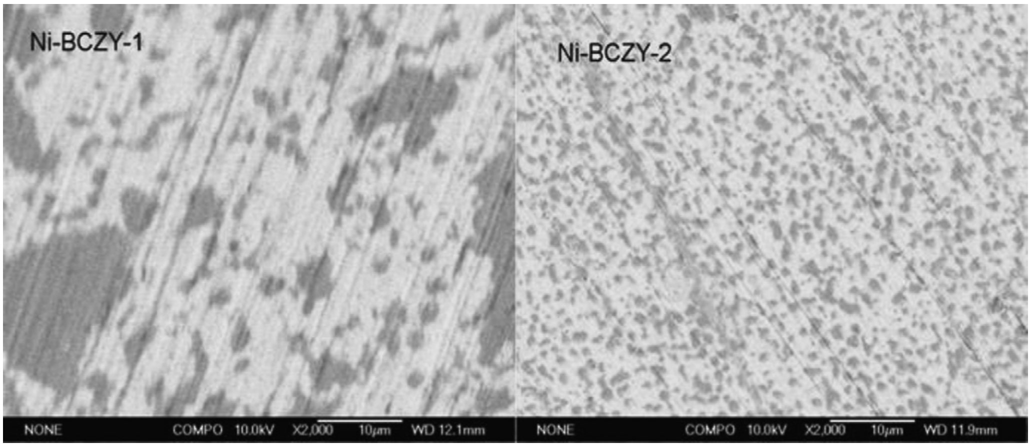

Fig. 4. Backscattered electron images of the cermet prepared by different methods.

the mixed powders prepared by the packing method. In the mean while, the reverse reaction of Eq. (1) would occur. $BaCO_3$ and Y doped CeO_2–ZrO_2 solutions would continue to react at elevated temperatures, as a result, the pure phase BCZY was obtained.

The relative densities of three different Ni–BCZY-2 cermets sintered at 1400 °C, 1350 °C and 1300 °C for 5 h are about 92.6%, 91.7% and 90.2%, respectively, but for Ni–BCZY-1 cermets sintered at 1400 °C for 5 h, the relatives densities is only about 79.1%. The relative densities of these three different Ni–BCZY-2 cermets are higher than that of Ni–BCZY-1 cermet. The sintering temperature of the cermet fabricated via the packing method can be reduced by 130 °C compared with that of the traditional method (1430 °C [7,8]). It can be concluded that the powders prepared via the packing method have better sinterability. This may be due to the ultra-fine grain size of powders prepared by the packing method.

Fig. 3 presents the EDS analysis of two different points in the Ni–BCZY-2, point 1 shows the analysis of the conglobation, indicating the main element of conglobation is Ni. Point 2 shows the analysis of the elemental composition around of conglobation, showing that this point contains a little Ni as well as the expected BCZY. From the results of EDS, it is concluded that the Ni phase was packed by the BCZY phase through the packing method.

The preparation method of cermets affected not only the powders size but also homogeneity of two phases. The morphology and phase distribution of cermets were characterized with BSEM and the results are shown in Fig. 4. The white areas are ceramic phase and the black areas are the metal phase [1,2,6,7]. Comparing the two images, it is easy to find that the uniformity of Ni–BCZY-2 is much better than that of Ni–BCZY-1.

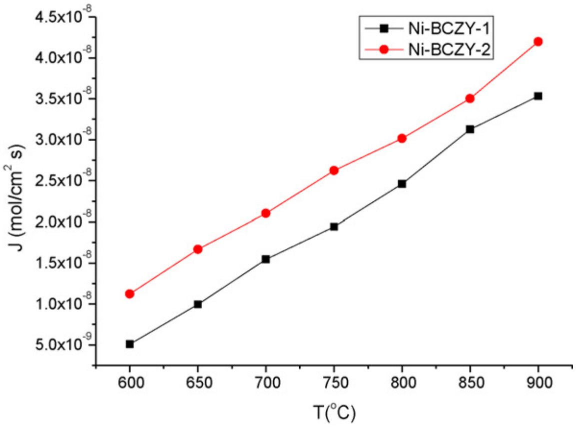

Fig. 5. Influence of temperatures on the hydrogen permeation fluxes through the cermet. Ar flow rate: 20 mL/min.

Fig. 5 shows the hydrogen flux as a function of temperatures for Ni–BCZY-1 and Ni–BCZY-2. The hydrogen permeation fluxes for all the samples increased with temperature from 600 °C to 900 °C. The Ni–BCZY-2 sample shows higher permeability than that of Ni–BCZY-1 at each fixed temperature. For the Ni–BCZY-2 sample, the hydrogen permeation fluxes were about 4.20×10^{-8} mol/cm^2 s at 900 °C, which was about 18% higher than that of Ni–BCZY-1 sample at the same temperature. The different performance can be explained by the concept of three-phase boundaries (TPB). From Fig. 4, obviously, the homogeneity of two phases for the Ni–BCZY-2 is better than that for the Ni–BCZY-1, and that would increase the hydrogen exchange rate on the surface of Ni–BCZY-2, resulting in a higher hydrogen permeation flux for Ni–BCZY-2. Another explanation is that the homogenous mixture of Ni and BCZY is geometrical better for proton transport as it provides more continuous route for proton. We calculated the values of activation energy (Ea) for these membranes through the hydrogen permeation fluxes. The permeation Ea of Ni–BCZY-1 is about 39.3 kJ/mol, whereas the Ea value is about 32.4 kJ/mol for Ni–BCZY-2. The difference of activation energy is due to the differences in surface exchange rate and the homogeneity.

4. Conclusions

The mechanical mixing powders method and the packing method were used to prepare the composite membranes. XRD showed that the metal phase of Ni was compatible with the perovskite phase BCZY and no new phase was detected for membranes derived from these two methods. The BSEM results showed that the cermet prepared by the packing method possessed a more uniform microstructure of the two mixed phases and better sintering ability. The hydrogen permeation flux of Ni–BCZY-2 was higher than that of Ni–BCZY-1 at each fixed temperature. Increasing surface exchange rate and proton diffusion would improve the hydrogen permeation performance.

Acknowledgements

This work was supported by National High-tech R&D Program of China (no. 2007AA05Z157) and Key Program of Chinese Academy of Sciences (no. KJCX1.YW07). W.P. Sun also acknowledges the CAS Special Grant for Postgraduate Research, Innovation and Practice.

References

[1] C.D. Zuo, S.E. Dorris, U. Balachandran, M.L. Liu, Chem. Mater. 18 (2006) 4647.
[2] C.D. Zuo, T.H. Lee, S.E. Dorris, U. Balachandran, M.L. Liu, J. Power Sources 159 (2006) 1291.
[3] D.E. NaNu, A.J. Bottger, J. Alloys Compd. 446 (2007) 571.
[4] S. Fang, L. Bi, L. Yan, W. Sun, C. Chen, W. Liu, J. Phys. Chem. C 114 (2010) 10986–10991.
[5] L. Yan, W. Sun, L. Bi, S. Fang, Z. Tao, W. Liu, Int. Hydrogen Energy 35 (2010) 4508–4511.
[6] C.D. Zuo, T.H. Lee, S.J. Song, L. Chen, S.E. Dorris, U. Balachandran, M.L. Liu, Electrochem. Solid-State Lett. 8 (2005) J35.
[7] S.M. Fang, L. Bi, X.S. Wu, H.Y. Gao, C.S. Chen, W. Liu, J. Power Sources 183 (2008) 126.
[8] S.M. Fang, L. Bi, C.L. Yang, L.T. Yan, C.S. Chen, W. Liu, J. Alloys Compd. 475 (2009) 935.
[9] X.F. Zhu, H.H.W.W.S. Yang, J. Membr. Sci. 309 (2008) 120.
[10] L. Chevalliar, M. Zunic, V. Esposito, E.D. Bartolomeo, E. Traversa, Solid State Ionics 180 (2009) 715.
[11] W. Sun, L. Yan, B. Lin, S. Zhang, W. Liu, J. Power Sources 195 (2010) 3155–3188.
[12] K.H. Ryu, S.M. Haile, Solid State Ionics 125 (1999) 355.
[13] F. Trobec, V. Thangaduai, Inorg. Chem. 47 (2008) 89720.