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Microstructure, mechanical and electrical properties of Ni-YSZ anode supported solid oxide fuel cells

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ABSTRACT

Purpose: Investigation of the Ni-YSZ cermets for anode supported solid oxide fuel cells (SOFC) prepared by uniaxial pressure, sintered and reduced pellets of NiO-YSZ.

Design/methodology/approach: Density examination, shrinkage examination, transverse rupture strength tests, microstructure examination.

Findings: Basing on the investigations of the anode Ni-YSZ type fabricated with powder metallurgy it was found of that density of sintered samples depends on NiO portion, temperature of sintering and reducing. Increase of sintering temperature causes increase of density. Moreover increase of NiO portion and reducing temperature causes decrease of density and linear contraction of anode.

Practical implications: The Ni-YSZ cermets fabricated using of powder metallurgy are characterized by very good properties and can be used as SOFC anode. Powder metallurgy gives the possibility to manufacturing cermet used as an anode for SOFC on the basis of Ni-YSZ.

Originality/value: Investigations of compacted, sintered and reduced samples with different amount of NiO gives information about optimal manufacturing conditions and volume fraction of NiO/YSZ components. This information is especially important at production process of extruded tubes.

Keywords: Composites; Powder metallurgy; Sintering; Mechanical and electrical properties

MATERIALS

1. Introduction

In general Fuel Cells are electrochemical conversion devices to produce electricity directly from fuel. Application of this or other modern energy production technology including solar energy plays important role for saving conventional fuel materials. In the particular case of Solid Oxide Fuel Cells (SOFC) all the main components (electrodes and electrolyte materials) are solids [1-3]. The conversion of chemical energy into electrical energy in a fuel cell was first demonstrated about 160 years ago. Both attractive system efficiencies and environmental benefits are associated with fuel-cell technology. They have proved some difficulties to develop early scientific experiments into commercially viable industrial products. The popular cermets of Ni–YSZ are applied as anode, which consists of three different phases such as: a metallic Ni, an YSZ ceramic and pores resulting in very complicated structural features. Moreover, manufacturing methods, particle-size distribution of a used powder, sintering and reducing conditions have a very important influence on the final properties of an anode [4-9].

There are two main variations of chemical composition used for anodes [10-15]. The most frequently used is 50/50% of Ni/YSZ one. Unfortunately the use of these compositions is not explained precisely. The aim of this investigation is an optimization of manufacturing conditions and chemical composition of anode supported SOFC manufactured on the basis of NiO and YSZ powders.

2. Material and research methodology

The investigated specimens were fabricated using commercial cubic YSZ ceramic powder, containing 8 mol% Y_2O_3 with an average particle size of 0.6μm and reported surface area of 7 m^2/g, produced by Tosoh Corporation, and NiO (black nickel oxide grade A, produced by INCO). Both type of powder were in agglomerate state (Figure 1). In order to improve the mixing and compacting process acetone with the micro wax were added. The mixture was mixed manually by pestle and mortar during 15 min in order to break the agglomerates. The portion of micro wax was 10% in volume, what improved the compatibility and porosity, after sintering. Volume fraction of NiO in relation to YSZ amount were from 10 to 90% with gradation every 10%. The mixture of powder was compacted in the uniaxial unilateral die. The diameter of green pellets was 11 mm and height not higher than 1 mm (Figure 2). The diameter of green parts for examination by three-point bending test was 31,5x13xx1 mm. Green parts were sintered at temperature of 1300, 1350, 1400 and 1450°C in muffle furnace under the air for 2 h.

The heating rate was not higher than 3°C/min. The reducing process was made in tubular furnace in the atmosphere of the flowing N_2-5%H_2 mixture of gases at temperature of 800, 900, 1000 and 1100°C. Density measurements were made using the Archimedes method basing on the product mass and the apparent loss of mass during immersion in water according to standard. Moreover, linear contraction of sintered and reduced samples was measured. In regard to small size of investigated samples the electrical properties were tested on the basis of resistance and next to calculate in conductance. The resistance was measured between two point (gold probes) at the surface of the pellet in 10th different areas for comparison among samples. Next the average and conductance were calculated. The flexural strength of sintered and reduced samples was examined by three-point bending test. Figure 2 shows a micrograph of investigated materials in compacted, sintered and reduced state.

3. Results and discussion

In a first step the sintering temperature of NiO-YSZ composite was optimized through density measurements resulting in 1400ºC (Figure 3). XRD patterns of NiO–YSZ composite before reduction and Ni–YSZ cermet after reduction, showed that before reduction, the sample consists of two phases, the cubic NiO and cubic YSZ. After being exposed to a reducing gas mixture at 800°C for about 5 h, the NiO in NiO/YSZ composite was reduced completely to metallic Ni. For the different compositions, shorter reducing times or higher thickness produced incompletely reduced samples which can be seen, at first glance as green areas. Figure 4 XRD shows patterns of reduced samples with different compositions. The intensity of Ni phase increases as the NiO content changes in the cermet. In all the cases no NiO peaks were found. In Fig. 5, the effect of reducing temperature on the shrinkage in samples sintered at 1400ºC is shown. For compositions less than 70%

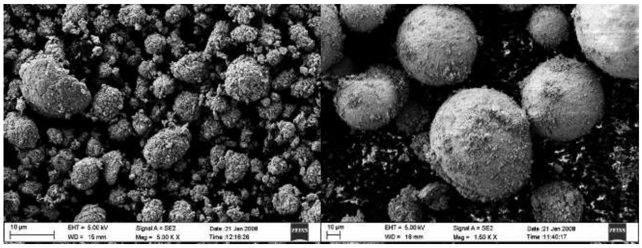

Fig. 1. SEM micrographs of (a) NiO and (b) YSZ powders

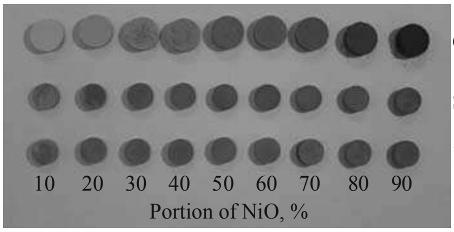

Fig. 2. Investigated samples in compacted, sintered an reduced state

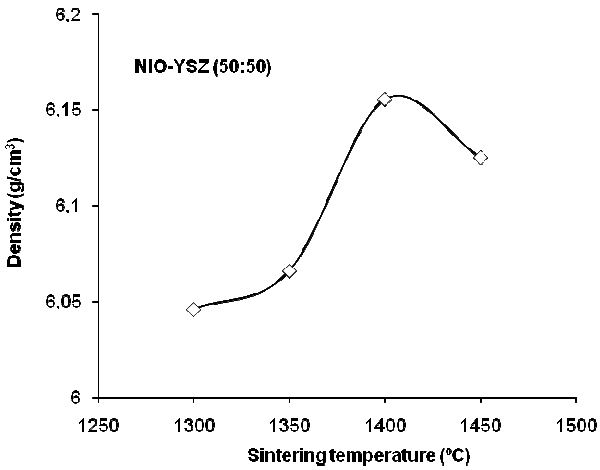

Fig. 3. Sintering curve of 50/50% in vol. NiO-YSZ composite

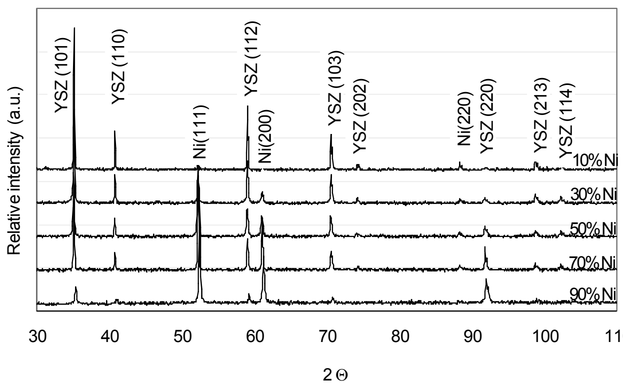

Fig. 4. XRD patterns of reduced samples (at 800ºC) with different amount of YSZ

of NiO the contraction remain basically constant with the reducing temperature due to the YSZ amount is high enough to keep a uninterrupted ceramic skeleton. However for higher amount of NiO the contraction of the samples is governed by the metallic component. Figure 6 shows the SEM images of some Ni-YSZ cermets. Due to particle size and the backscattered coefficients of Ni and YSZ phases were too much alike, it was very difficult to differentiate each phase in Ni–YSZ cermets via optical or scanning electron microscopy. Nevertheless the presence of Ni was demonstrated by point analysis by EDS in different particles. The morphology analysis seems indicate that sintering temperature should not be higher than 1400ºC. Independently on the NiO portion sintering at the temperature of 1450ºC produce growth and coagulation of grain what is shown in Fig. 6. Moreover it was found out that relative homogeneous microstructure with local large grains were characteristic for materials with NiO portion in range from 50% to 70%. The anodes sintered at temperature of 1450ºC with the lower than 50% or higher than 70% NiO portion characterize lower porosity (Fig. 6a). On the basis of density examination of sintered at 1400ºC and reduced at 800°C samples it was found out that apparent density of cermets were highest than theoretical density of NiO-YSZ composites as a consequence of density difference between Ni in relation to NiO. Taking into account this densities measured by Archimedes method and the absolute density estimated by He pycnometer, open porosity was calculated. Open porosity of Ni-YSZ cermets sintered at 1400ºC and reduced at 800ºC are displayed in Figure 7. As expected the porosity increases with NiO content as a consequence of their reduction to metallic Ni. This effect is favorable for the transport of fuel gas in the anode materials. However, when the level of porosity is too high mechanical properties decrease. On the basis of electrical properties investigation it was found out that independently on sintering and reducing temperature increasing NiO portion causes the increase the conductance in Ni-YSZ cermet. Relation between conductance and NiO portion is shown in Fig. 8.

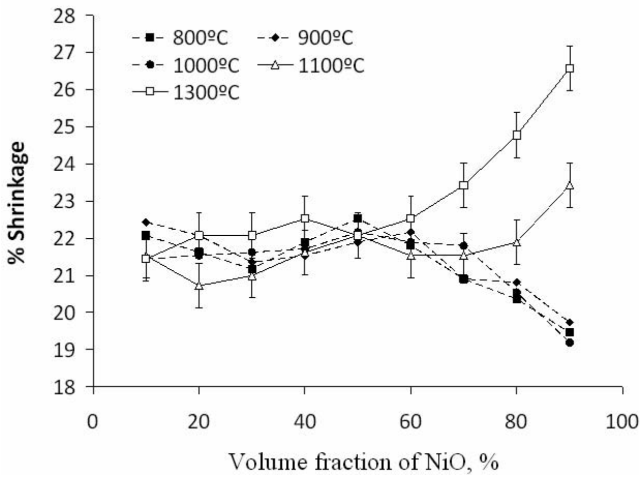

Fig. 5. Shrinkage in relation to reducing temperature for samples sintered at 1400ºC with different volume fraction of NiO.

Lower than 40% portion of NiO produce relative low conductance and exclude application of this material as a anode material in SOFC. Mechanical properties of sintered and reduced parts deduced from the three point bending test are presented in Figure 8.

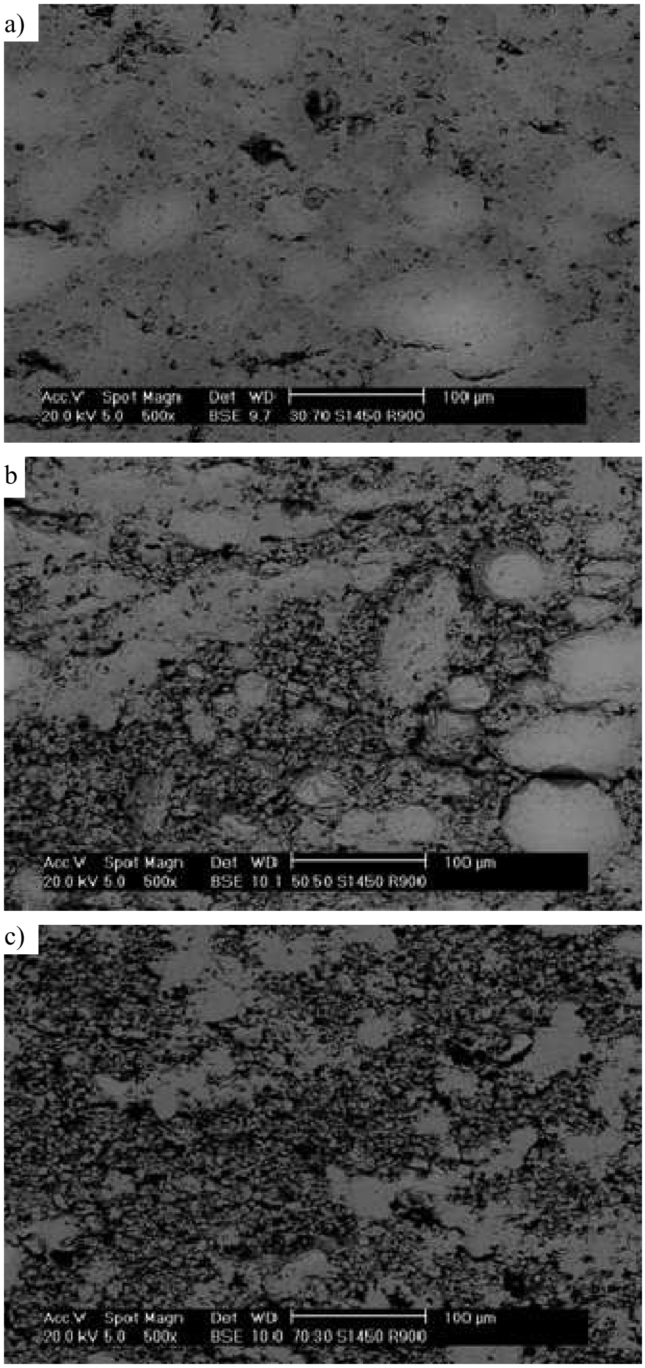

Fig. 6. Structure of samples sintered at 1450°C and reduced at 900°C a)30%, b)50% and c)70% of NiO

The investigation was made for samples with the 40 to 90% NiO portion because material with less than 40% portion of NiO have poor electrical properties. It was found that the increase of NiO portion decrease the mechanical properties of anode as a consequence of the increase of porosity. In order to keep a relative high mechanical properties required for an anode supported SOFC, the amount of NiO in the NiO-YSZ composite should not be higher than 60%.

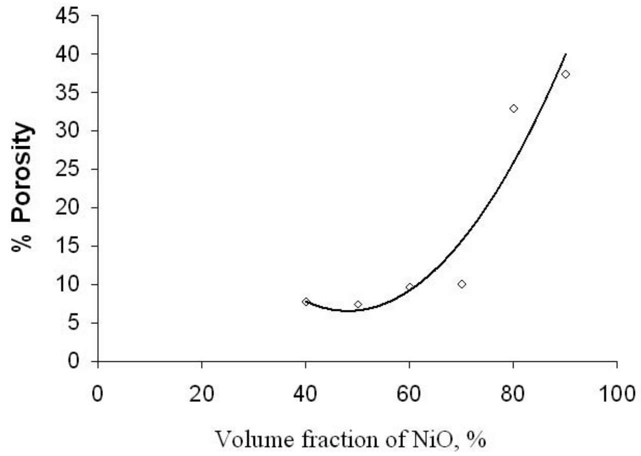

Fig. 7. Open porosity as a function of volume fraction of NiO

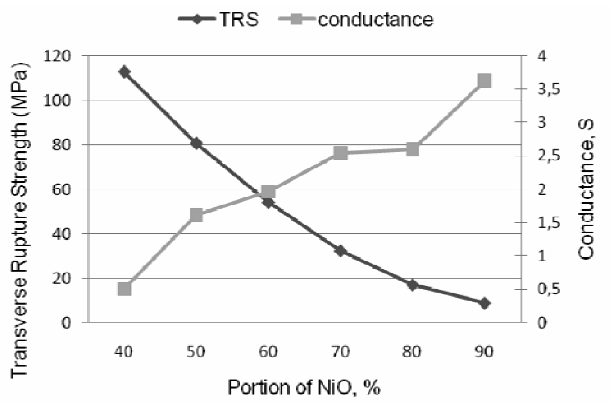

Fig. 8. Mechanical and electrical properties versus volume fraction of NiO

4. Conclusions

NiO-YSZ composites with different amount of NiO have been prepared by uniaxial compaction. Different sintering and reducing treatment has been performed in order to obtain the optimum composition and treatment for an anode supporting SOFC. The best sintering temperature for all compositions was 1400ºC and full reduction of NiO took place at the lowest tested temperature (800ºC). Homogeneity of the different Ni-YSZ cermets was evaluated by SEM. The porosity of the samples increases with the amount of NiO, and changes between 10-15% for intermediate compositions and rise up to 40% for samples with the highest Ni content. Finally, it was found that NiO content in the composite should not be less than about 40% in volume, because of lower values produces a relative high resistivity, inadmissible for anode materials. Moreover NiO portion should not be higher than about 60% in order to keep relative high mechanical properties.

Acknowledgements

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References

[1] F. Tietz, Materials selection for Solid Oxide Fuel Cells, Materials Science Forum 426-432 (2003) 4465-4470.

[2] B.C.H. Steele, A. Heinzel, Materials for fuel-cell technologies, Nature 414 (2001) 345-352.

[3] L.A. Dobrzański, L. Wosińska, B. Dołżańska, A. Drygała, Comparison of electrical characteristics of silicon solar cells, Journal of Achievements in Materials and Manufacturing Engineering, 18 (2006) 215-218.

[4] S. Tekeli, A. Akçimen, O. Gürdal, M. Gürü, Microstructural and electric al conductivity properties of cubic zirconia doped with various amount of titania, Journal of Achievements in Materials and Manufacturing Engineering, 25/2 (2007) 39-43.

[5] G. Dercz, K. Prusik, L. Pająk, Structure investigations of commercial zirconia ceramic powder, Journal of Achievements in Materials and Manufacturing Engineering, 18 (2006) 259-262.

[6] J.H. Yu, G.W. Park, S. Lee, S.K. Woo, Microstructural effects on the electrical and mechanical properties of Ni-YSZ cermet for SOFC anode, Journal of Powder Sources 163 (2007) 962-932.

[7] M. Gaudon, N.H. Menzler, E. Djurado, H.P. Buchkremer, YSZ electrolyte of anode-supported SOFCs prepared from sub micron YSZ powders, Journal of Materials Science 40 (2005) 3735-3743.

[8] Y. Du, N.M. Sammes, Fabrication and properties of anode-supported tubular solid oxide fuel cells, Journal of Power Sources 136 (2004) 66-71.

[9] Y. Du, N.M. Sammes, G.A. Tompsett, Optimisation parameters for the extrusion of thin YSZ tubes for SOFC electrolytes, Journal of the European Ceramic Society 20 (2000) 959-965.

[10] J.J. Sun, W.Y. Choi, H.E. Kim, Y.H. Koh, Fabrication and characterization of YSZ/Ni-YSZ bi layered composites using thermoplastic coextrusion, Material Chemistry and Physics 104 (2007) 288-292.

[11] D.-S. Lee, J.-H. Lee, J. Kim, H.-W. Lee, H.S. Song, Tuning of the microstructure and electrical properties of SOFC anode via compaction pressure control during forming, Solid State Ionics 166 (2004) 13-17.

[12] K.R. Lee, S.H. Choi, J. Kim, H.-W. Lee, J.-H. Lee, Viable image analyzing method to characterize the microstructure and the properties of the Ni/YSZ cermet anode of SOFC, Journal of Power Sources 140 (2005) 226-234.

[13] S.-D. Kim, H. Moon, S.-H. Hyun, J. Moon, J. Kim, H.-W. Lee, Ni-YSZ cermet anode fabricated from NiO-YSZ composite powder for high-performance and durability of solid oxide fuel cells, Solid State Ionics 178 (2007) 1304-1309.

[14] F. Tietz, F.J. Dias, D. Simwonis, D. Stöver, Evaluation of commercial nickel oxide powders for components in solid oxide fuel cells, Journal of the European Ceramic Society 20 (2000) 1023-1034.

[15] Ch. Lee, J. Bae, Fabrication and characterization of metal-supported solid oxide fuel cells, Journal of Power Sources 176 (2008) 62-69.