ELSEVIER

Journal of Alloys and Compounds 449 (2008) 331–334

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

The effect of ball milling parameters and Ni concentration on a YSZ-coated Ni composite for a high temperature electrolysis cathode

Hyun Seon Hong *, Ui-Seok Chae, Soo-Tae Choo

Plant Engineering Center, Institute for Advanced Engineering (IAE), Yongin 449-863, Republic of Korea

Received 4 November 2005; received in revised form 14 December 2005; accepted 3 January 2006
Available online 22 January 2007

Abstract

Ni/YSZ composite powders used as the cathode material for high temperature electrolysis were synthesized by the ball milling of Ni and YSZ powders. The effect of ball milling parameters and Ni concentration on microstructure of Ni/YSZ composite powders were investigated. The electrical conductivity of the composite was measured to examine its relationship with microstructure. Microstructural analysis of the ball-milled powder showed that YSZ particles were finely distributed over the surfaces of nickel particles and that the nickel particles appeared to be interconnected. This interconnection creates an electrically conductive pathway at room temperature. The conductive pathway was less developed at higher YSZ concentrations due to surface coverage of Ni surfaces by YSZ particles. Electrochemical properties of the composites were investigated high temperature electrolysis.

Keywords: High temperature electrolysis; Cathode material; Ni/YSZ cermet; Hydrogen production; SOFC

1. Introduction

High temperature electrolysis (HTE) may become a technology capable of producing hydrogen for a future hydrogen economy. This technology is based upon the partial replacement of electricity with thermal energy for the electrolysis [1–8]. External heat sources such as solar, nuclear or integrated gasification combined cycle can partially replace electricity in an electrolysis reaction. Although most HTE research remains at the laboratory scale, its potential efficiency and the ability to use external heat sources have generated a great deal of interest in HTE for its application as a hydrogen production system.

A nickel and yttria stabilized zirconia composite (Ni/YSZ cermet) is currently the preferred cathode material for HTE or solid oxide fuel cells (SOFC) since Ni and YSZ are relatively cheap compared to Pt and chemically stable in a H_2O/H_2 mixture over a wide temperature range [2,9–12]. Many studies show that the performance and electrical properties of Ni/YSZ cermet are dependent on the microstructures and distribution of Ni and YSZ particles in the composite. Alternatively, characteristics of the starting powders and fabrication process are important for Ni/YSZ cermet properties.

The Ni/YSZ cermet is conventionally made by milling and sintering of NiO and YSZ powders followed by reduction on exposure to hydrogen gas. A large density difference between Ni and YSZ prevents the milling of Ni and YSZ powder. High energy ball milling or mechanical alloying is a process that can be used to produce composite materials from a blend of elemental or alloy starting materials. In recent years, this technique has been used to make a wide range of materials including metal/oxide composites from elements that have different densities or melting point temperatures [13,14]. In this study, modified Ni/YSZ cermets for HTE were directly synthesized by the ball milling of Ni and YSZ powders. Ball milling was carried out in a dry process and in a wet process with varying milling times. The effect of the ball milling on the microstructure of the composite was examined and the relationship between the microstructure and electrical conductivity at room temperature was investigated.

2. Experimental

The Ni/YSZ composite materials were synthesized by ball milling of Ni and YSZ powders. Nickel (Kojungdo Chem., average particle size of 2 μm) and

* Corresponding author. Tel.: +82 31 330 7481; fax: +82 31 330 7113.
E-mail address: hshong@iae.re.kr (H.S. Hong).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2006.01.131

Table 1
Electrical conductivity of Ni/YSZ composites at room temperature

Composite	Method	YSZ content (vol%)	Average electrical conductivity ($S\,cm^{-1}$)	
			After milling	After sintering[a]
Ni/YSZ	Dry	60	1.8×10^{-7}	$<10^{-5}$
	Wet[b]	60	1.9×10	2.5×10^2
		40	2.5×10^2	1.0×10^4

[a] At 900 °C for 2 h under vacuum.
[b] In ethanol.

8 mol% Y_2O_3 stabilized ZrO_2 (YSZ, Tosoh Co., average particle size of 0.2 μm) were used as starting materials. The volume ratio of Ni to YSZ was controlled to be between 0.4 and 0.6. The ball milling media (Fritsch, Pulverisette 6) consisted of ZrO_2 balls (2 mm in diameter) and a ZrO_2 bowl (250 cm^3). The ball to powder weight ratio was 15 to 1 and the rotating speed was 250 rpm.

Composites were formed by dry (w/o ethanol) and wet ball milling (w/ethanol). In the dry process, 0.1 wt% stearic acid powder ($CH_3(CH_2)_{16}COOH$, 0.1 wt%) was used as a process control agent (PCA) to reduce clumping at the initial milling stage. The ball-milled powder was pressed into a disc with 10 mm diameter and 1 mm thickness. After pressing, discs were sintered at 900 °C for 2 h in a vacuum to prevent the oxidation of specimens. For the wet process, the raw materials were ball-milled in the zirconia bowl, into which 200 cm^3 of ethanol was added. The wet ball-milled powders were baked at 60 °C for 4 h. Discs were pressed from the baked powder, sintered at 900 °C for 2 h and then used for electrical conductivity measurements. Electrical conductivity measurements of the dry and wet ball-milled sintered specimens were done at room temperature by the four point probe method.

The morphology and phase identification of the composites were determined by scanning electron microscopy with energy dispersive analysis of X-rays in each step of the cermet synthesis process. Crystal structure of the composite was determined by X-ray diffractometry. Particle size distribution was determined by the laser diffraction and scattering method.

3. Results and discussion

Fig. 1 shows the XRD patterns of dry and wet ball-milled Ni/YSZ composites. The XRD pattern for the specimen formed by the dry ball milling method indicated that the composite powder was composed of crystalline Ni and YSZ particles. The pattern did not change with the increase in milling time from 3 to 24 h. Similar XRD patterns were observed for wet ball milling. The composite consisted of crystalline Ni and YSZ particles. Milling time up to 24 h did not affect the XRD pattern.

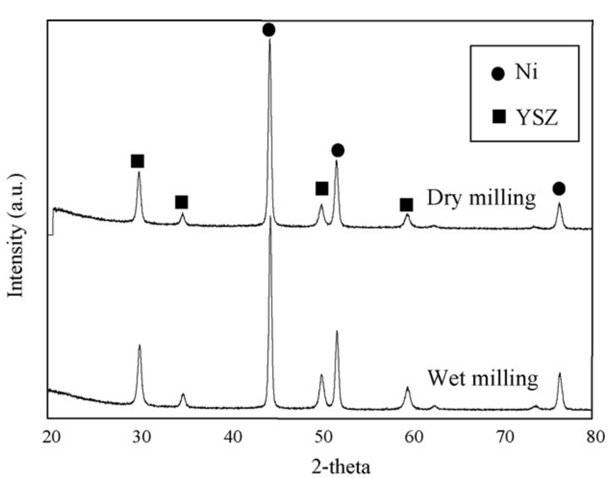

Fig. 1. XRD patterns of dry- and wet-milled Ni/YSZ composites.

The electrical conductivities of the Ni/YSZ composites measured at room temperature are listed in Table 1. The electrical conductivity of the wet ball-milled (in ethanol) Ni/YSZ composite was about $5 \times 10^2\ S\,cm^{-1}$ while the Ni/YSZ composite fabricated dry had a much lower value of $1.6 \times 10^{-7}\ S\,cm^{-1}$. A possible explanation for the large difference in electrical conductivity may be due to the different morphologies of the dry and wet ball-milled Ni/YSZ composites. Fig. 2a shows that YSZ particles are randomly distributed over the surface of the Ni particles of the wet ball-milled composite. This is in contrast to the surface of the Ni particles of the dry ball-milled composite

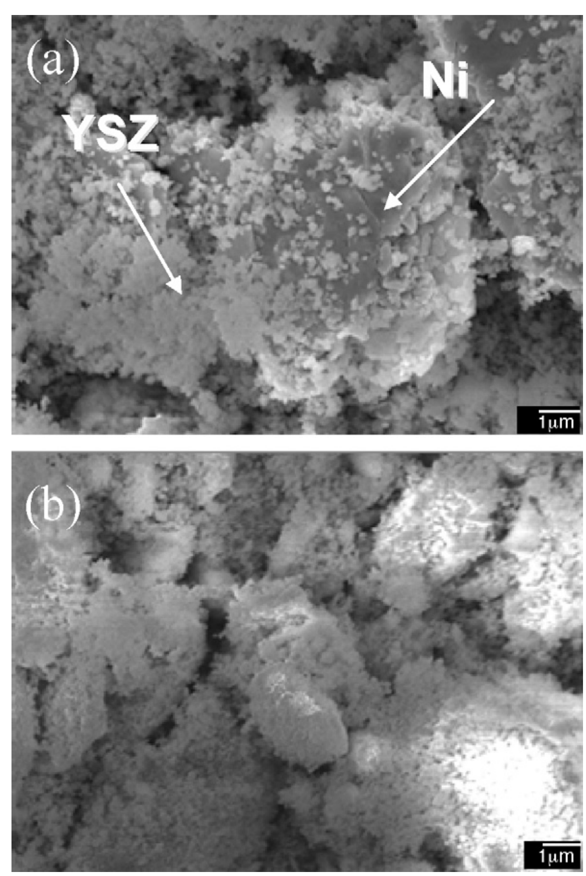

Fig. 2. SEM images of Ni and Ni/YSZ composite powders: (a) dry-milled Ni/YSZ and (b) wet-milled Ni/YSZ.