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Characteristics of Ni/YSZ Cermet Prepared by Mechanical Alloying Method for the High Temperature Electrolysis of Steam

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ABSTRACT

Ni/YSZ (Y_2O_3-stabilized ZrO_2) composite as an electrode component for High Temperature Electrolysis (HTE) was fabricated by mechanical alloying method using Ni and YSZ powders. Characterization of the synthesized composite was investigated with various analysis tools, including XRD, SEM and PSA, and a self-supporting planar unit cell prepared with the Ni/YSZ composite was prepared to study the electrochemical reactions for the production of hydrogen. The Ni/YSZ cermet is composed of crystalline Ni and YSZ, in a sub-micro scale, and has an even distribution without aggregated particles. In addition, under an electrochemical reaction, the unit cell showed an H_2 evolution rate from steam of 14 Nml/min and 600 mA/cm^2 of current density at the electrode.

Key words : HTE, Hydrogen, Ni/YSZ, Mechanical alloying, Electrolyte

1. Introduction

Hydrogen is currently made from fossil fuels by steam reforming and the partial oxidation of natural gas or oil fractions. However, these processes emit greenhouse gases into the environment. Therefore, other methods of hydrogen production that do not use fossil fuels and produce less greenhouse gases should be considered. An alternative process is High-Temperature Electrolysis (HTE) in which electrical energy is used without the production of pollutants. Furthermore, HTE can produce hydrogen using less electric power than conventional water electrolysis, and the ceramic solid-oxide cell for HTE is nearly free from corrosion.[1-3] The process is particularly attractive when external heat sources are used (e.g., solar, nuclear, or integrated gasification combined cycle) to promote the splitting of water molecules.[4,5]

Ni/YSZ (8 mol% Y_2O_3-stabilized ZrO_2) composite powder is currently the most common cathode material for HTE due to its low cost and chemical stability in H_2O/H_2 mixture.[6] The Ni/YSZ cermet is conventionally prepared by reduction of the NiO/YSZ composite fabricated from NiO and YSZ, because of the large density difference between Ni and YSZ. Mechanical alloying or high energy ball milling is a process that can be used to produce nanocrystalline alloy and composite materials from a blend of elemental or alloy starting powders.[1,2,7] Milling parameters such as the milling time and rotation speed affect not only the grain size of the as-milled alloy, but also the thermal stability of the given grain.[7] In this study, Ni/YSZ cermets for HTE and SOFC are synthesized by the high energy ball milling of Ni and YSZ powders. Characterization of the synthesized composite is investigated using various analysis tools including XRD, SEM and PSA, and a self-supporting planar unit cell prepared with the Ni/YSZ composite was prepared to study electrochemical reactions for production of hydrogen.

2. Experimental Procedure

2.1. Preparation of the Ni/YSZ Composite

The Ni/YSZ composites were directly prepared by high energy ball milling (Fritsch, Pulverisette 6) of Ni and YSZ powders in terpineol. Nickel (Kojungdo Chem., average particle size of 2 μm) and 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 0.6. The grinding media (Fritsch, Pulverisette 6) consisted of ZrO_2 balls (2 mm in diameter) and a ZrO_2 bowl (250 cm^3). Details of the milling conditions and preparation process are described in Table 1 and Fig. 1.

The raw materials were ball-milled in a zirconia bowl with terpineol. The wet ball-milled powders were baked at 60°C for 4 h. The morphology of the composite particles was observed by Scanning Electron Microscopy (SEM). The crystal structure of the composite was determined by X-Ray Diffractometry (XRD). The Particle Size Distribution (PSD) was determined by a laser diffraction and scattering method.

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Table 1. The MA Conditions Adopted in the Present Study of Ni/YSZ Cermet

MA parameters	Milling time (h)	Rotation speed (rpm)	Ball-powder weight ratio
A	24	250	15:1
B	48	400	
C	90		

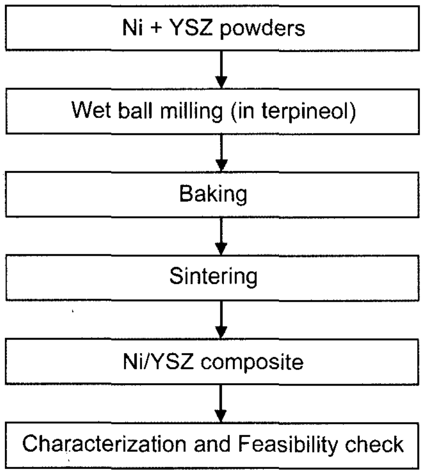

Fig. 1. Schematic diagram of the preparation procedure for the Ni/YSZ composite.

2.2. Measurement of High Temperature Electrochemical Reaction

Fig. 2 shows a schematic diagram of the self-supporting planar unit cell and the electrolysis apparatus. The cell consists of an electrolyte plate of YSZ and porous electrodes. The YSZ disk is a plate with a thickness of 0.5 mm, and electrodes were printed on an area of 3.14 cm^2 with a thickness of less than 0.03 mm. The cathode material is Ni/YSZ, and the anode consists of Pt paste. Ni/YSZ cermet and Pt pastes were silk-printed on back of a YSZ disk and sintered at 1450°C for 2 h. Argon was used as a carrier gas, and was controlled with a mass-flow controller. The carrier gas was mixed with steam was supplied inside the electrolysis cell. The hydrogen concentration was measured at the outlet of the cathode compartment by gas chromatography (HP 5890 Series II). The electrolysis electric power was supplied by a DC power supply (Solatron 1287 potentiostat). The heating rate of the electric furnace temperature was set so that it was less than 5°C/h.

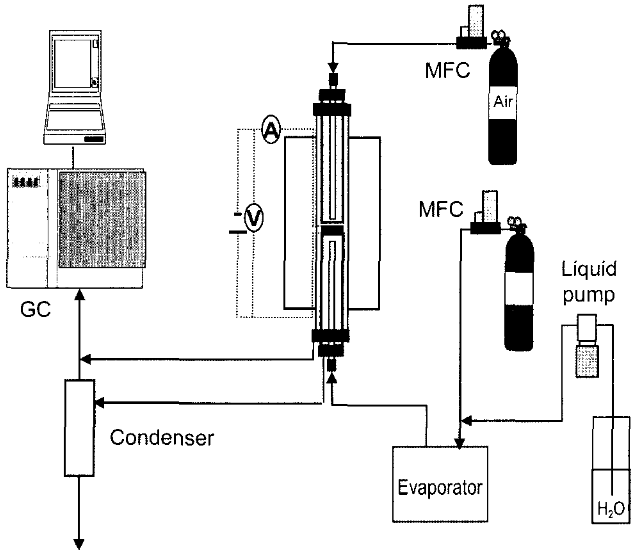

Fig. 2. Schematic diagram of the experimental apparatus for the high temperature electrochemical reaction.

3. Results and Discussions

3.1. Morphology of Ni/YSZ Composites According to the Ball Milling Energy

XRD patterns of the Ni/YSZ composites as a function of the milling time or rotation speed are shown in Fig. 3. The XRD patterns show that the ball-milled composites at various milling times and rotation speeds were composed of crystalline Ni and YSZ. Fig. 3(a) reveals no changes with an increase in milling time from 24 to 90 h. Fig. 3(b) shows that a rotation speed up to 400 rpm does not influence the composite phase.

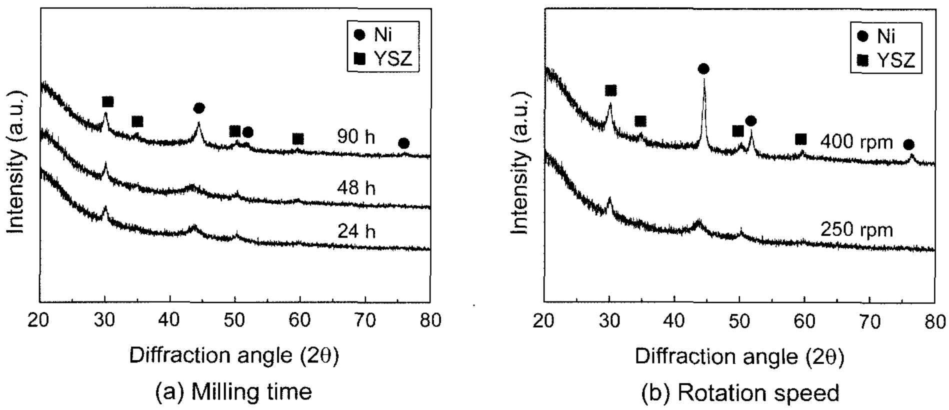

Fig. 3. XRD patterns of the Ni/YSZ composites as function.

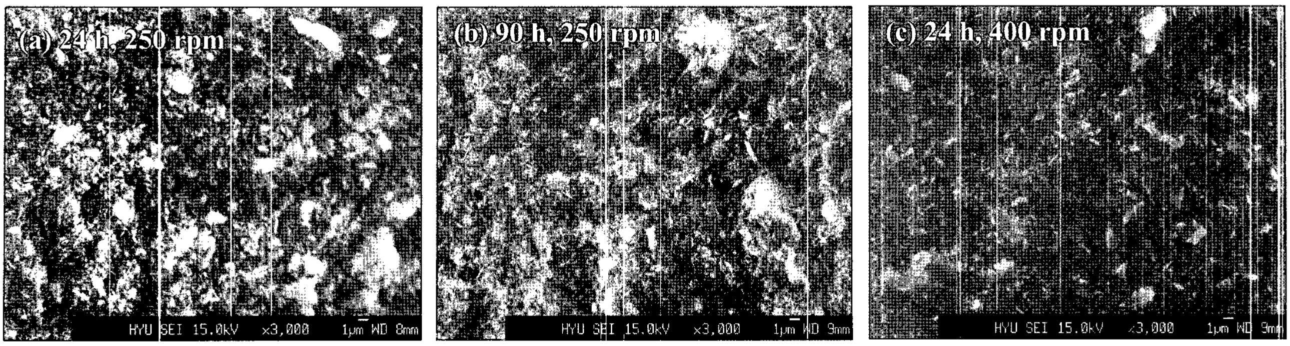

Fig. 4. SEM images of ball-milled Ni/YSZ composite in various conditions.

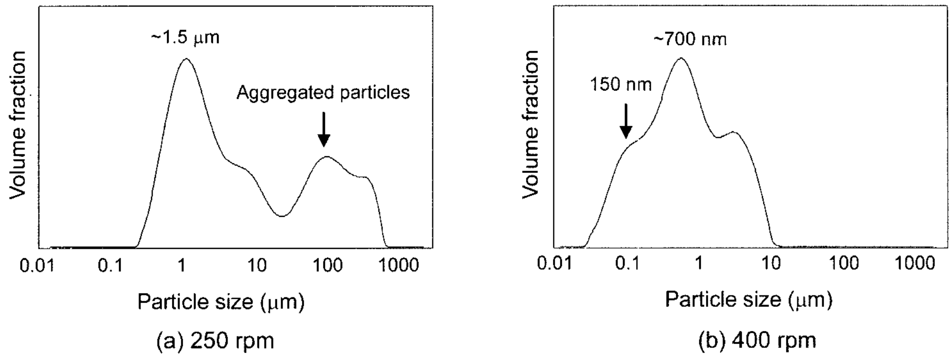

Fig. 5. Particle size distribution of the Ni/YSZ powders.

The morphology of the Ni/YSZ composite prepared by ball milling with various milling times and rotation speeds is presented in Fig. 4. The shape of the particles is non-spherical and the average particle size ranges from approximately 700 nm to 1500 nm, which is smaller than the starting Ni powder material. As the milling time is increased, there is little change in the average particle size of the ball-milled composites. However, as the rotation speed increases to 400 rpm, the average particle size of the ball-milled Ni/YSZ composite decreases from 1500 nm to 700 nm. This suggests that an increase in the rotation speed influences the value of the minimum grain size attained by ball milling.[8]

Fig. 5 shows the particle size distribution measured by laser diffraction and scattering. Fig. 5(a) shows that the ball-milled powder with a rotation speed of 250 rpm has a broad particle size distribution and mainly consists of particles around 1.5 μm and aggregated particles around 100 μm. On the other hand, as the rotation speed is increased to 400 rpm, the ball-milled powder has a narrow particle size distribution of approximately 700 nm and aggregated particles are not observed. This may have resulted because the powders are repeatedly flattened, welded and fractured during ball milling.[9]

3.2. Hydrogen Production by High Temperature Electrolysis

Fig. 6 shows the relationship between the current density and the hydrogen production from Ni/YSZ composites

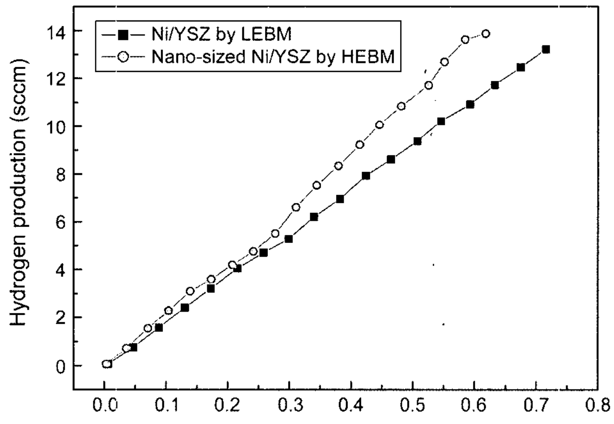

Fig. 6. Relationship between the current density and hydrogen production.

prepared by LEBM (Low Energy Ball Milling) at 250 rpm and HEBM (High Energy Ball Milling) at 400 rpm. The maximum hydrogen production rate of nano-sized Ni/YSZ by HEBM is 14 Nml/min with 0.6 A/cm^2 at 800°C, which is higher than that of the Ni/YSZ composite by LEBM. This result is likely due to the fact that the high energy ball milling increases the Triple-Phase-Boundary (TPB) of the Ni/YSZ composite. The relationship can be characterized by stating that the hydrogen production is a linear function of the current density.[3] The microscopic structure analysis of prepared unit cell is under way, as a future study.

4. Conclusions

A nano-sized Ni/YSZ composite was successfully fabricated by the ball milling of Ni and YSZ powders. These crystallites were milled time for 90 h. Ball milling parameters such as the milling time and the rotation speed influenced the average particle size of the Ni/YSZ composites. As the milling time was increased, there was little change in the particle size of the composites. However, as the rotation speed increased, the particle size of Ni/YSZ composite decreased and the Ni/YSZ particles were uniformly distributed without aggregated particles. A possible explanation for the refined microstructure was that the increase in the rotation speed minimized the particle size by causing the particles to become more finely milled and fractured. A self-supporting planar cell was fabricated in order to improve hydrogen production performance. In an electrolysis experiment with the planar cell, hydrogen could be produced at a maximum production rate of 14 Nml/min under an electrolysis temperature of 800°C. The nano-sized Ni/YSZ composite prepared by high energy ball milling increased the hydrogen production performance.

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