

Microstructure and electrical conductivity of Ni/YSZ and NiO/YSZ composites for high-temperature electrolysis prepared by mechanical alloying

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Abstract

Nickel and yttria stabilized zirconia (Ni/YSZ) composite powders for a cathode that can be used in high-temperature electrolysis are synthesized by the ball milling of Ni and YSZ powder and by the ball-milling of NiO and YSZ powder. The influence of ball milling parameters such as milling environment and milling time on the microstructure and electrical conductivity are investigated. Microstructural analysis of the ball-milled powder shows that the milling time and environment affect the crystal structure and particle size of the composites. A NiO/YSZ composite composed of crystalline NiO and YSZ particles changed to an amorphous phase after milling for 90 h. As the milling time is increased, there is little change in the particle size of dry-milled powder whereas the particle size decreases with wet-milled powder. After subsequent cold-pressing and annealing at 900 °C for 2 h, the particle size is increased in the wet-milled powder. The electrical conductivity increases after sintering at 900 °C. Well-connected particles are thought to be the reason for the enhanced electron conductivity after sintering. © 2005 Elsevier B.V. All rights reserved.

Keywords: High-temperature electrolysis; Cathode material; Nickel/yttria stabilized zirconia composite; Hydrogen production; Electrical conductivity; Particle size

1. Introduction

At present, hydrogen is mainly produced by the steam reforming of natural gas. This process, however, releases large amounts of carbon dioxide. Therefore, other methods of hydrogen production that do not use fossil fuels and emit less or zero carbon dioxide should be considered. A possible approach is high-temperature electrolysis (HTE) in which electrical energy is used without the emission of pollutants. In addition, HTE offers the prospect of a high overall energy efficiency [1–6]. 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 [7,8]. The promising level of 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 for fuel cells.

A nickel and yttria stabilized zirconia composite (Ni/YSZ cermet) is presently the preferred cathode material for HTE since Ni and YSZ are relatively cheap compared with a platinum alternative, immiscible with each other, and chemically stable over a wide range of temperature [2,9–12]. Conventionally, the Ni/YSZ cermet is prepared by the sintering of NiO and YSZ powders, followed by reduction on exposure to hydrogen gas. The large difference in density between Ni and YSZ prevents the direct sintering of Ni and YSZ powder. High energy ball milling or mechanical alloying can be used to produce composite materials from a blend of elemental or alloy starting powders. This type of method was originally developed to produce oxide dispersion strengthened nickel-based alloys. In recent years, however, the technique

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has been used to make a wide range of materials that include metal/oxide composites from elements that are immiscible in the liquid state, have different melting point temperatures, or have different densities [13,14].

In this study, modified Ni/YSZ cermets for HTE have been directly synthesized by the ball milling of Ni and YSZ powder or NiO and YSZ powder, followed by the reduction of NiO. Ball milling is carried out in a dry process or in ethanol, with varying milling times. The influence of milling environment and milling time on the microstructure and electrical conductivity of the Ni/YSZ cermets at room temperature is investigated.

2. Experimental

2.1. Ni/YSZ cermet from Ni and YSZ powder

To make a Ni/YSZ cermet, Ni and YSZ powders were mechanically processed in a planetary ball mill (Fritsch, Pulverisette 6). Nickel (Kojungdo Chemicals; average particle size: 63 μm) and 8 mol% Y_2O_3 stabilized ZrO_2 (YSZ, Tosoh Co.; average particle size: 0.2 μm) were used as starting materials. The volume ratio of Ni to YSZ was 0.6. The grinding media consisted of ZrO_2 balls (2 mm in diameter) and a ZrO_2 bowl. The ball-to-powder weight ratio was 15 and the rotating speed was 280 rpm. In order to prevent contamination, powder charging and withdrawing was performed in a glove box under an argon atmosphere.

Ball milling was conducted either in a dry condition or in ethanol (wet condition). In the dry process, 0.1 wt.% stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, 0.1 wt.%) was used as a process control agent (PCA) to reduce excessive welding of the powder at the initial milling stage. Ball-milled powder from the dry process was pressed into a disc with a diameter of 10 mm and the thickness of 1 mm. After pressing, discs were sintered at 900 $^\circ\text{C}$ for 2 h. The sintering was performed in a vacuum to prevent the oxidation of specimens. The electrical conductivity of the pressed and sintered specimens was measured by the four-probe point method at room temperature. For the wet process, the ball-milled powder in ethanol was baked at 60 $^\circ\text{C}$ for 4 h. The baked powder was pressed into discs and sintered at 900 $^\circ\text{C}$ for 2 h.

2.2. Ni/YSZ cermet from NiO and YSZ powder

For comparison, Ni/YSZ cermet was synthesized from NiO and YSZ powder. NiO (Kojungdo Chemicals; average particle size: 0.3 μm) and 8 mol% Y_2O_3 stabilized ZrO_2 (YSZ, Tosoh Co.; average particle size: 0.2 μm) were used as starting materials. The NiO and YSZ powders were ball-milled either in a dry condition or in ethanol, and then pressed and sintered at 900 $^\circ\text{C}$ for 2 h. The cermet was prepared similarly, but the additional heat treatment for the reduction of NiO/YSZ cermet was carried out at 900 $^\circ\text{C}$ for 2 h in a hydrogen atmosphere after sintering. The electrical conductivity of

the reduced cermet from the wet process was compared with that from the dry process.

2.3. Measurements

The morphology of the composite particles was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with energy dispersive analysis (EDS) of X-rays in each step of the cermet synthesis process. The crystal structure of the prepared composite was determined by X-ray diffractometry, and the particle-size distribution was obtained by means of the laser diffraction and scattering method.

3. Results and discussion

3.1. Ni/YSZ cermet from Ni and YSZ powder

X-ray diffraction patterns for the Ni/YSZ composite milled in a dry process or in ethanol for various milling times are shown in Fig. 1. The pattern for the dry process reveals that the composite is composed of crystalline Ni and YSZ particles and the pattern does not change with an increase in milling time from 3 to 48 h. The XRD pattern for the wet process shows that the composite also consists of Ni and YSZ

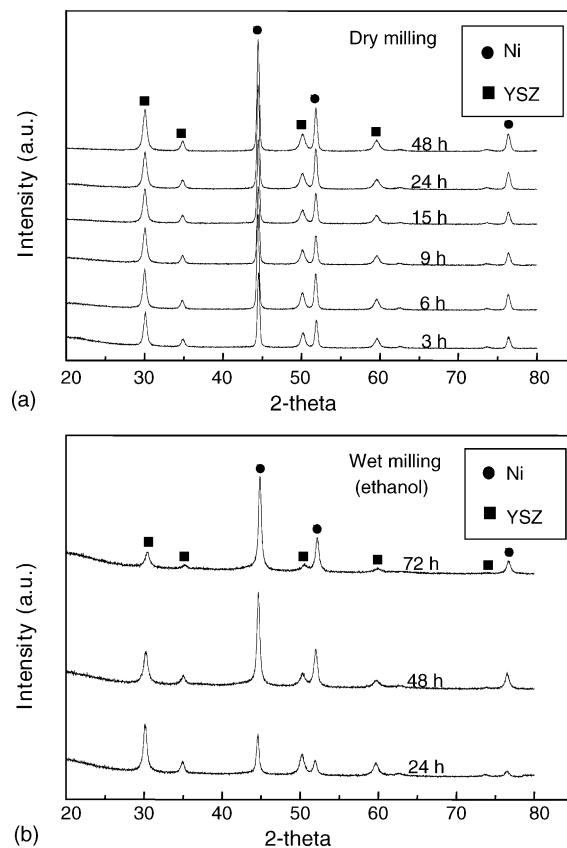


Fig. 1. XRD patterns for Ni/YSZ composites as function of milling time: (a) dry milling; (b) wet milling.

particles and a milling time of up to 72 h does not influence the composite phase.

The morphology of the Ni/YSZ composite produced by dry ball milling with different milling times is presented in Fig. 2. The particles are spherical and the average particle size ranges from 65 to 80 μm , which is slightly larger than the starting Ni powder material. There is little change in the com-

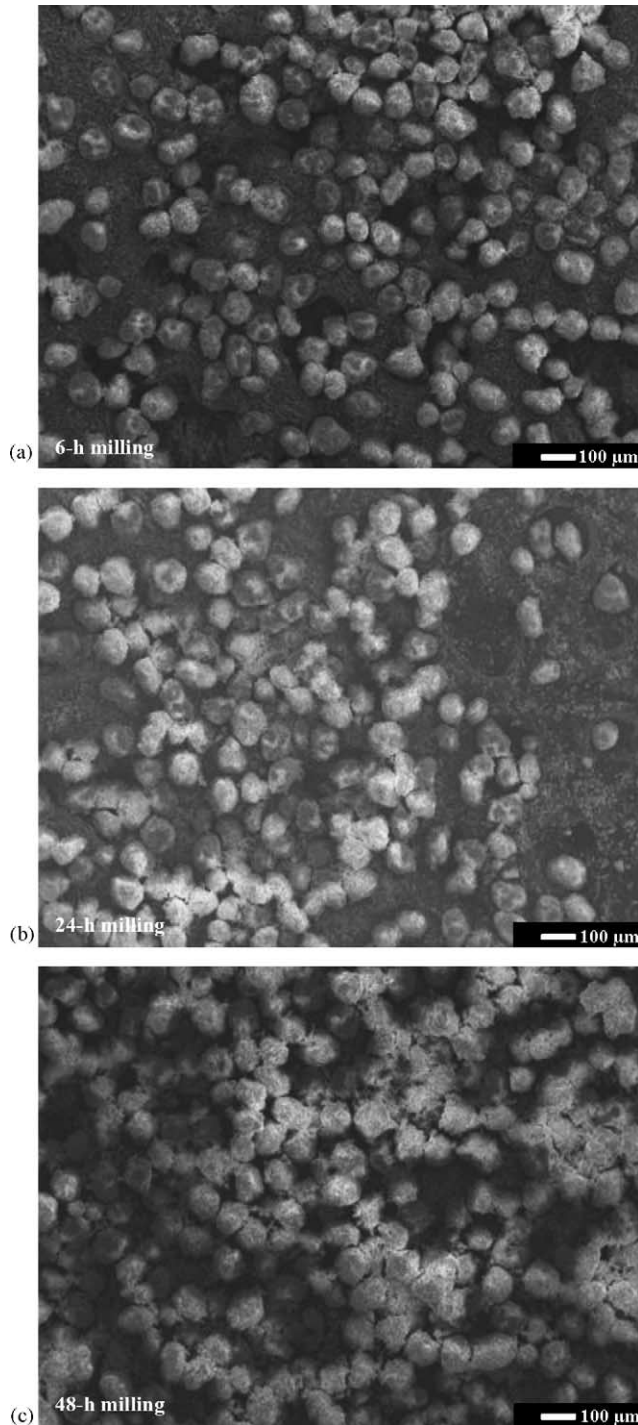


Fig. 2. Scanning electron micrographs of Ni/YSZ composite by dry milling: (a) 6 h; (b) 24 h; (c) 48 h.

posite particle size with increase in milling time. Scanning electron micrographs of Ni/YSZ composite particles milled in ethanol for 24 and 48 h, are given in Fig. 3(a) and (b), respectively. The average particle size is around 10 μm in the 24 h milled sample, and is smaller than that of the dry-milled powder. It is to be noted that very fine particles of less than 200 nm are also observed in TEM analysis. The particles are

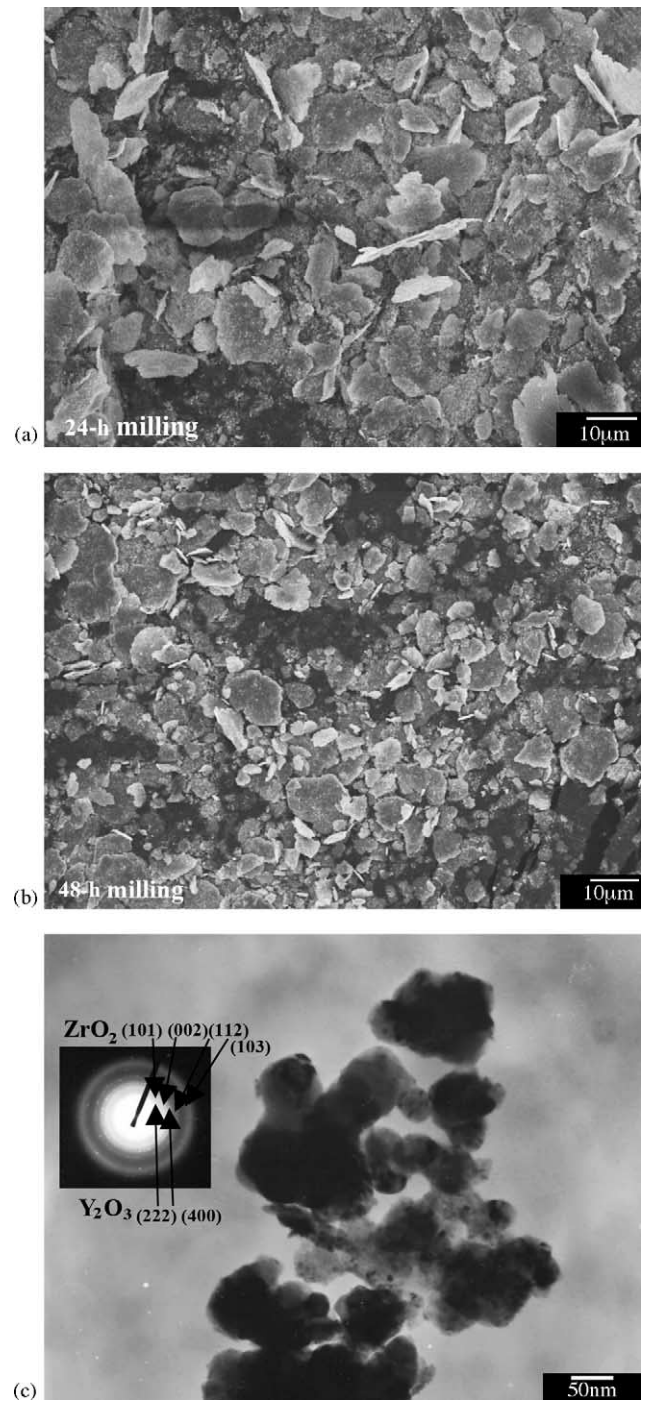


Fig. 3. Scanning electron micrographs of Ni/YSZ composite by wet milling: (a) 24 h; (b) 48 h; (c) transmission electron micrographs of 24 h milled composite.

identified as YSZ particles by TEM pattern analysis, as seen in Fig. 3(c), EDS investigation revealed that a small amount of Ni (around 5 wt.%) is dissolved in these fine YSZ particles.

As the milling time is increased to 48 h, the particle size further decreases. This may be because the powders are repeatedly flattened, welded and fractured during ball milling [13–15]. In this process, ethanol appears to coat the surface of particles and disturb the welding step so that fragmented particles can be obtained and decrease the average particle size. The shape of some particles is non-spherical since ball milling for 48 h is not sufficient for equilibrium to be reached. The stearic acid (0.1 wt.%) added in the dry process reduces the excessive welding of particles but does not appear to affect a reduction in particle size.

3.2. Ni/YSZ cermet from NiO and YSZ powder

X-ray diffraction patterns for the NiO/YSZ composite milled in a dry process or in ethanol are shown in Fig. 4. The patterns for dry-ball milling reveal that after 6 and 24 h of millings, the composite consists of crystalline NiO and YSZ particles. As the milling time is increased to 90 h, the composite changes to an amorphous phase, as seen in Fig. 4(a). The XRD patterns of the 24 h milled powder produced either by the dry or by the wet process are presented in Fig. 4(b). Both the composites consist of NiO and YSZ particles. Ethanol

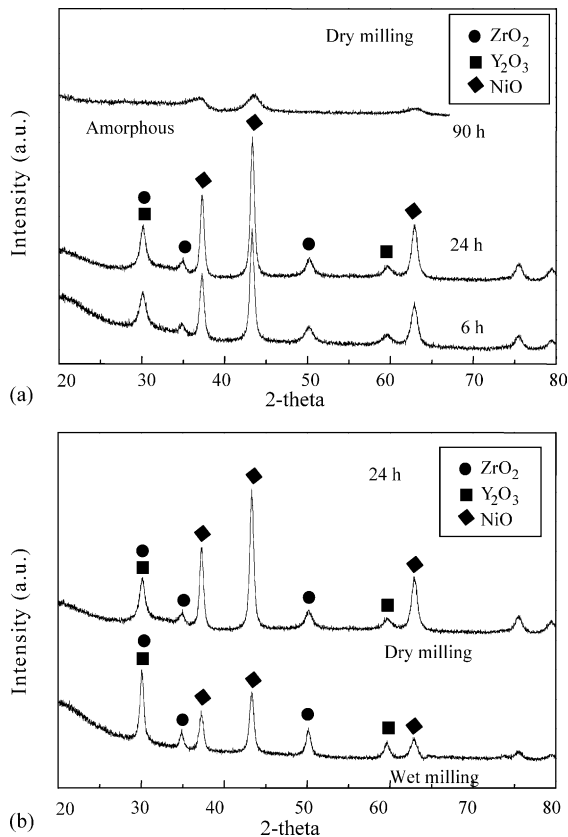


Fig. 4. X-ray diffraction patterns of NiO/YSZ composite as function of: (a) milling time; (b) milling conditions.

and stearic acid used in the wet milling do not influence the crystal structure of NiO and YSZ.

The morphology and the particle-size distribution of the NiO/YSZ composite milled for 24 h are presented in Fig. 5. The dry ball-milled composite particles are spherical with an average particle size of around 750 nm, which is larger than that of the raw NiO powder. The wet-milled samples have an average particle size of around 225 nm, which is smaller than that of dry-milled powder. TEM and EDS analyses reveal that particles larger than 300 nm are a mixture of NiO and YSZ powders when powders are milled in the dry condition (Fig. 6). On the other hand, the particles of the NiO

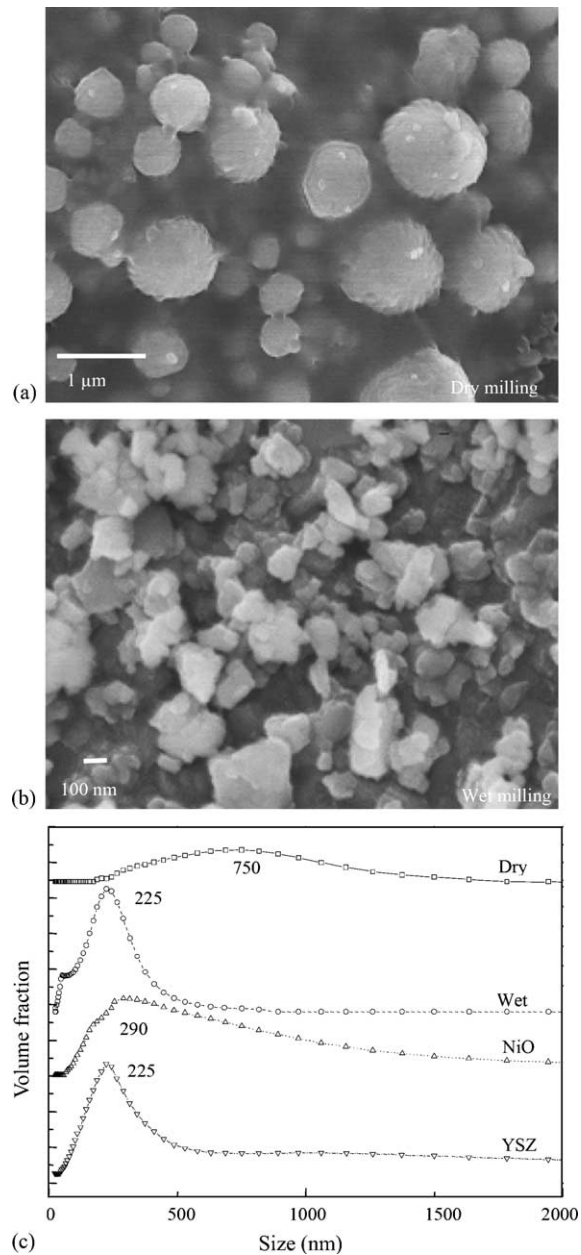


Fig. 5. Scanning electron micrographs of Ni/YSZ composite and particles-size distribution of powders: (a) dry milling; (b) wet milling; (c) size distribution.

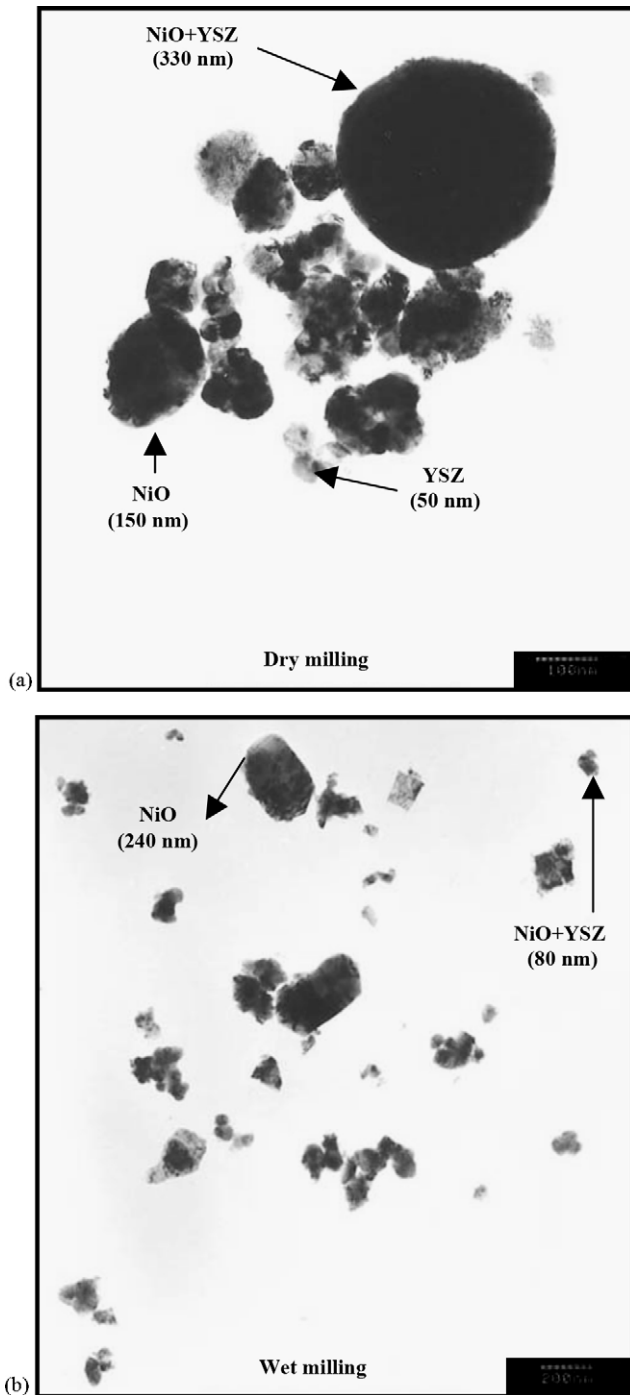


Fig. 6. Transmission electron micrographs of Ni/YSZ composite: (a) dry milling; (b) wet milling.

and YSZ mixture are smaller than those of the raw materials (225–290 nm) in wet milling.

3.3. Electrical conductivity

The electrical conductivities of the Ni/YSZ and NiO/YSZ composites measured by the four-point probe technique at room temperature are listed in Table 1. The electrical conduc-

Table 1

Electrical conductivity of Ni/YSZ and NiO/YSZ composites at room temperature

Composite	Method	Average electrical conductivity ($\times 10^3 \text{ S cm}^{-1}$)		
		After milling	After sintering ^a	After reduction ^b
Ni/YSZ	Wet	0.5	14	–
NiO/YSZ	Dry	Negligible ^c	Negligible	0.5
	Wet	Negligible	Negligible	0.5

^a At 900 °C for 2 h under vacuum.

^b At 90 °C for 2 h under H₂ atmosphere.

^c $<10^{-7} \text{ S cm}^{-1}$.

tivity of the Ni/YSZ composite ball-milled powder in the wet condition is around $5 \times 10^2 \text{ S cm}^{-1}$ and this value increases to $1.4 \times 10^4 \text{ S cm}^{-1}$ after sintering at 900 °C. Little change in particle size is observed after sintering. Nevertheless, the particles became denser due to closer packing and this can provide better electron migration paths. Thus, closer contact of the particles is a possible explanation for the enhanced electron conductivity after sintering.

The electrical conductivity of the NiO/YSZ composite ball-milled powder in the wet and dry condition is very low, namely, less than $10^{-7} \text{ S cm}^{-1}$. After reducing the NiO/YSZ composites at 900 °C for 2 h under hydrogen, the electrical conductivity increases to $5.0 \times 10^2 \text{ S cm}^{-1}$. Examination by XRD confirms that NiO is changed to Ni after the reduction.

4. Conclusions

Ni/YSZ cermets are successfully synthesized directly by the ball milling of Ni and YSZ powder, and also by the balling of NiO and YSZ powder with subsequent reduction of the NiO powder at 900 °C. The Ni/YSZ composite consists of crystalline Ni and YSZ particles. Similarly, the NiO/YSZ composite is composed of crystalline NiO and YSZ particles. These crystallites are maintained for a milling time of 72 h.

Milling process control agents such as stearic acid and ethanol influence the average particle size of the composites. Dry milling increases the particle size, whereas wet milling decreases the size. Wet milling reduces the average particle size by producing fragmented particles. As the milling time is increased, the particle size of the composites decreases during wet milling.

Sintering produces only a minimal change in particle size, but enhances the electrical conductivity of the powders. A possible explanation for the enhanced electron conductivity is that sintering creates better electron migration paths by causing the particles to become denser and more closely packed.

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