Microstructural effects on the electrical and mechanical properties of Ni–YSZ cermet for SOFC anode

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Abstract

The electrical and mechanical properties of Ni–YSZ cermet as the anode support of solid oxide fuel cell (SOFC) are determined by the metallic and ceramic components, respectively. We used YSZ and NiO commercial powders of the average particle size from 1 to 10 μm to fabricate Ni–YSZ cermets with different microstructures. The porosity of the cermets was also modified by the amount of carbon black addition. The distribution of each phase of cermets was analyzed with scanning electron microscopy combined with energy dispersive spectroscopy. The electrical conductivity and fracture strength of the Ni–YSZ cermets were investigated and interpreted in a view of percolation phenomena. The finer particles, either NiO or YSZ, were interlinked well by sintering and the electrical and mechanical properties of Ni–YSZ cermets were enhanced by the percolation of Ni and YSZ, respectively.
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1. Introduction

Solid oxide fuel cells (SOFCs) are the most efficient device generating electricity by electrochemically converting the chemical fuels such as hydrogen, methane, and synthetic gas into electricity. The feasibility of SOFCs has been presented from a few watts up to hundreds of kW for distributed power generation. The application of SOFC systems to kW-scaled auxiliary power unit (APU) has attracted increasing interest especially for the transportation market. For the APU systems, the fuel cell stack, including single cells, separators, and sealants, has to be compact in size to be equipped in vehicles and highly resistant to thermal and mechanical shock as well since the vehicles start up within tens of minutes [1]. Tubular-type SOFCs are being considered for APU due to its high mechanical and chemical stability over planar-type [2]. The electrode support, which sustains mechanical stress on the single cell, has porous microstructure so as to effectively transfer fuel gases to the interfaces with electrolyte and eliminate water vapor produced during the operation. High electrical conductivity is also an essential feature of the anode

material as primary current collector especially for tubular-type SOFCs where the electric current flows along the tubular electrode. Thus, the electrode support must have high electrical and mechanical strength despite its porous structure.

Ni–YSZ cermet has been successfully applied to either tubular- or planar-type of anode-supporting single cells [3,4]. Structural stability of the cermet is controlled by the porous framework of YSZ, of which mechanical properties has been gaining attention as well as its high ionic conductivity. Thus, the fracture strength of Ni–YSZ cermet would increase with increasing the content of YSZ. The electrical resistance of the cermet, however, would also increase with the volumetric fraction of YSZ since the electrical conductivity of the cermet is determined by the percolation of metallic nickel phase [5]. Therefore, it is necessary to make the anode support material highly conductive without sacrificing mechanical strength.

The authors postulate that the electrical and mechanical properties of the cermets could be tuned by controlling microstructure. According to the percolation theory, the electrical conductivity of two-phase composite is determined the size and shape of particles as well as volumetric fraction [6]. Finer conductive particles tend to be percolated through the composite material at lower concentration, which is called percolation threshold. Porosity of the composite is another factor to modify

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the percolation concentration as well [7]. The volumetric pores can be regarded as third insulating phase and the effective volume of conductive phase, e.g., Ni in Ni–YSZ cermet, decreases.

In this study, we modified the microstructure of Ni–YSZ cermet by using different types of commercial powders, NiO and YSZ, while fixed the volumetric ratio of Ni and YSZ to be 40:60. Commercial NiO powders has been already evaluated as a component of SOFC anode by other researchers [8], however, the performance of the anode material needs to be more precisely interpreted in a view of microstructure. Since the sinterability of starting powders also affects porosity of composite, the amount of carbon black addition was changed to modify the microstructures. In the previous work, several types of carbons were used to increase porosity and the carbon was oxidized over 600 °C remaining pores inside of NiO–YSZ after sintering [9]. We investigated the electrical and mechanical properties of Ni–YSZ cermets correlated with microstructure, which was strongly dependent on the size of starting powders.

2. Experimental

Commercial NiO and YSZ powders of different particle sizes were used to make NiO–YSZ composites and subsequently Ni–YSZ cermets by reducing with gaseous hydrogen. The average particle size of starting powders (d_{50}) were analyzed with a particle size analyzer (Fritsch GmbH, Analysette 22, Germany) and given in Table 1. Fine (MPC-ZY8, $d_{50} \sim 0.762$ μm) and coarse (MPC-ZY8C, $d_{50} \sim 7.798$ μm) 8YSZ powders commonly fabricated by Millennium Corp. were used while five different NiO powders were classified to three coarse-class ones of the average particle size over 5 μm and two fine-class ones below 1 μm. Fine 8YSZ powder was mixed with coarse and fine NiO powders to make FC-series and FF-series composites, respectively. Coarser 8YSZ powder was also mixed with fine NiO powders (CF-series) to modify the microstructure. The

mixing ratio of NiO and YSZ was fixed to 55:45 for all the cermets after reduction to contain 40 vol% Ni. The addition of 13 or 40 vol% carbon black (LG carbon, L30, Korea) changed the relative sintered density as well.

The mixture of NiO, YSZ, and certain amount of carbon black was wet-milled for 24 h and dried. Disk- and square-shaped samples were prepared by uniaxially pressing the powders at 400 kgf cm⁻² followed by sintering at 1400 °C for 3 h. The sintered samples were cut into bars for electrical and mechanical characterization. The bulk density of NiO–YSZ composite was measured by Archimedean method. Ni–YSZ cermet specimens were prepared by reducing the sintered oxide composites at 900 °C in H₂ gas. The microstructures of the as-sintered and reduced samples were characterized by scanning electron microscopy (FE-SEM, Hitachi S-4700, Japan). NiO (or Ni) and YSZ phases from the micrographs were also identified by energy dispersive spectrometer (EDS) and thus the distribution of each phase could be analyzed.

Four-probe dc method was used to characterize the electrical properties of metallic Ni–YSZ cermets. Under the operating condition of SOFCs, nickel oxide in NiO–YSZ composite is reduced to nickel and thus the anode shows metallic behavior. For reliable contact with lead wires, Pt paste (Engelhard, part no. 6926, U.S.A.) was applied to the sample and cured at 900 °C for 1 h. The samples were exposed to 10% H₂ (balanced with Ar) in a measurement cell and heated to the temperature of interest. Current–voltage characteristics were measured in the current range of −0.2 to 0.2 A using a Source-Meter (Keithley, K2400, U.S.A.). All the samples showed nearly linear I–V curves and the electrical resistance were obtained from the slope of curve by the least square method.

Fracture strength of Ni–YSZ cermet was evaluated with bar specimens by a 3-point flexure method. Bar specimens with nominal dimension of 2.5 mm × 3 mm × 25 mm were cut from the sintered block and edge-chamfered. The surface subjected

Table 1

The sample notation, the commercial powders (NiO and YSZ), the amount of carbon black added as a pore former, and the relative sintered density of NiO–YSZ composites used in this study (all the samples were sintered at 1400 °C)

8YSZ		NiO		Carbon black addition (vol%)	Sample notation	Relative sintered density (%)
Starting powders	Average particle size (μm)	Starting powders	Average particle size (μm)			
Fine class		Coarse class				
Millennium, MPC-ZY8	0.762	Junsei	6.789	13	FC1-13	86 (66)*
				40	FC1-40	76
		Aldrich-green	5.006	40	FC2-40	77 (60)*
		Aldrich-black	9.964	40	FC3-40	74
Fine class		Fine class				
Millennium, MPC-ZY8	0.762	High purity chemicals	0.878	13	FF1-13	91 (71)*
				40	FF1-40	86
		Baker	0.839	13	FF2-13	88 (70)*
Coarse class		Fine class				
Millennium, MPC-ZY8C	7.798	High purity chemicals	0.878	13	CF1-13	79 (59)*
		Baker	0.839	13	CF2-13	70
				40	CF2-40	61 (48)*

* Relative bulk density of Ni–YSZ cermet prepared by reducing NiO–YSZ composite.

to tensile stress during a flexure test was polished to 0.1 µm finish. The test was done using a universal testing machine (Hounsfield, S-series, U.K.) with a fixture of 25.4 mm span, at a constant crosshead speed of 3 mm min^{-1} at room temperature. The highest value and the lowest value were excluded from the calculations of average value and standard deviation of the fracture strength.

3. Results and discussion

3.1. Microstructure

The microstructures of FC2-40 and FF2-40 specimens, which were fabricated by sintering the mixture of fine YSZ powder and coarse or fine NiO powders, respectively, and the distribution of NiO grains were analyzed by FE-SEM combined with EDAX as shown in Fig. 1. The microstructure of NiO–YSZ composite was apparently controlled by the characteristics of starting powders. The use of coarse NiO powders (FC2-40 in Fig. 1a) made coarse NiO grains after sintering and the size of NiO grains in FC2-40 was nearly identical to the average particle size of NiO powder (~5 µm) analyzed by the particle size analyzer. We found from the preliminary experiments on the powder morphology that the particles of coarse NiO powders were mostly agglomerated by partial sintering. The strongly agglomerated particles

would not be easily ground by normal wet milling process and thus make coarse NiO grains in NiO–YSZ composites as sintered. On the contrary, fine NiO particles were dispersed better after the sintering as shown in Fig. 1b (FF2-40). In this case, the more homogeneous mixing of two powders could make finer microstructure after sintering. Since the solubility limits between NiO and YSZ are less than 2 mol% [10,11], the growth of each phase would be inhibited by the alien particles around. Fine NiO grains in the specimen FF2-40 were homogeneously dispersed and connected with neighboring NiO particles.

Fig. 2 shows the microstructure of Ni–YSZ cermets prepared by reducing NiO–YSZ composites in gaseous H$_2$. The distribution of Ni phase in Ni–YSZ cermet seems to be determined by the microstructure of NiO–YSZ composite. Coarse Ni particles in FC1-13, which had been composed of coarse NiO and fine YSZ grains before the reduction, were isolated by fine YSZ particles (Fig. 2a), while fine Ni particles in FF2-13 were well dispersed and interconnected to each other as shown in Fig. 2b. The microstructure made by YSZ grains was strongly dependent on the average particle size of YSZ powders as well. Coarse YSZ powders used to prepare CF-series specimens caused the coarser microstructure, which contained coarse YSZ grains mostly surrounded by fine Ni particles (Fig. 2c). The isolated YSZ grains in CF2-40 were kept from sintering, while Ni particles were interconnected along the surface of YSZ grains.
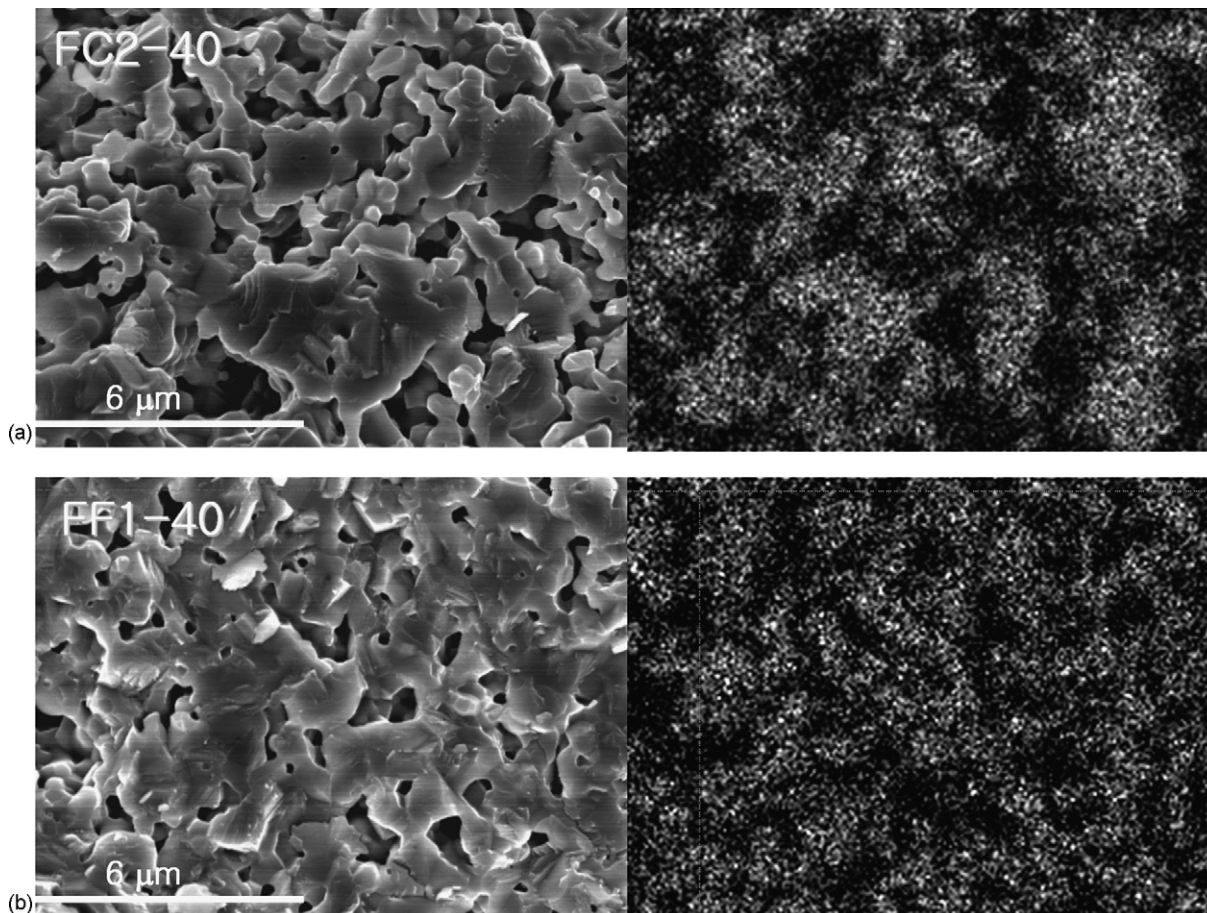

Fig. 1. Microstructure of NiO–YSZ composites prepared from (a) fine YSZ–coarse NiO:FC2-40 and (b) fine YSZ–fine NiO:FF1-40 mixtures with 40 vol% carbon black addition. Distributions of NiO grains were analyzed by EDS of Ni and presented on the right.
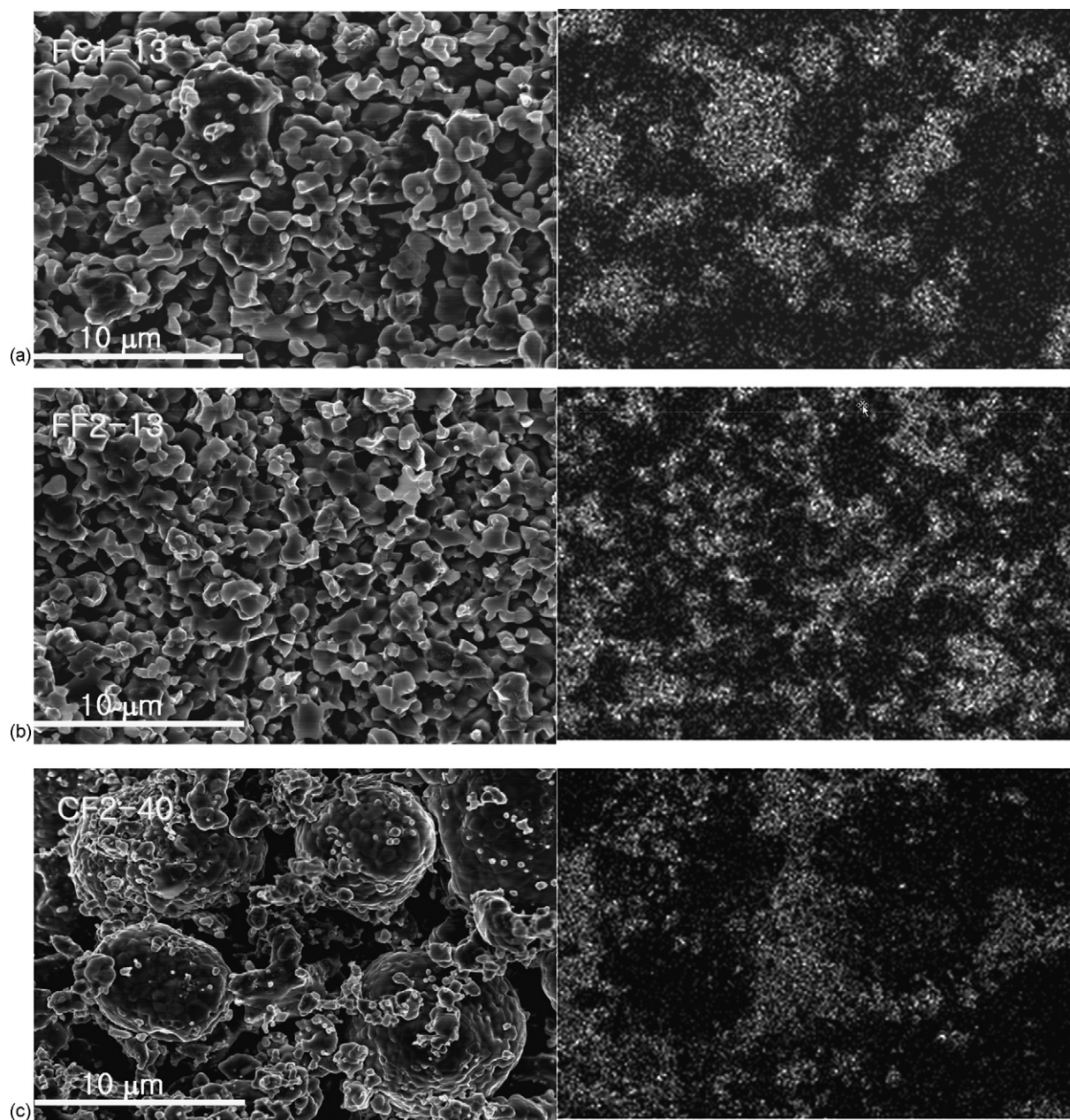
Fig. 2. SEM micrographs of Ni–YSZ cermets prepared by reducing (a) fine YSZ–coarse NiO:FC1-13, (b) fine YSZ–fine NiO:FF2-13, and (c) coarse YSZ–fine NiO:CF2-40 composites with the addition of 13 or 40 vol% carbon black. The distributions of Ni phase was analyzed by EDS of Ni and presented on the right.

Fig. 3 shows the relative bulk density of Ni–YSZ cermets prepared by reduction as a function of the relative sintered density of NiO–YSZ composites. As the dimensional change by reduction is assumed to be negligible, the relative bulk density of Ni–YSZ cermet (d_{Ni-YSZ}) would be 77% of that of NiO–YSZ ($d_{NiO-YSZ}$) containing 55 vol% NiO due to the difference in molar volume of NiO ($11.2\,cm^3\,mol^{-1}$) and Ni ($6.6\,cm^3\,mol^{-1}$). The relative densities of the samples were nearly consistent with the simulated values (solid line). This indicates that the framework of YSZ grains was not changed by reducing procedure but the porosity increased due to the volumetric change by the reduction of nickel oxide to nickel.

Starting powders considerably affect on the sintered density (or porosity) of NiO–YSZ composite and thus that of Ni–YSZ

cermet as given in Table 1. FF-series specimens, that were prepared with fine NiO and YSZ powders showed the relative sintered density about 90% while the composites with coarse powders, either NiO or YSZ (CF- and FC-series), showed relatively low sintered density. The increase of carbon addition as a pore former increased the porosity as well. The extent of increment in porosity by carbon addition, however, was dependent on the staring material. As the amount of carbon black increased from 13 to 40 vol%, the relative sintered density of FC1 and CF2 specimens decreased about 10% while that of FF1 showed only 5% decrease. It is because the sintering behavior of NiO–YSZ composites is also related to the percolation of each phase. Sintering means densification of material and adhesion of particles by mass transports through gas phases and/or by
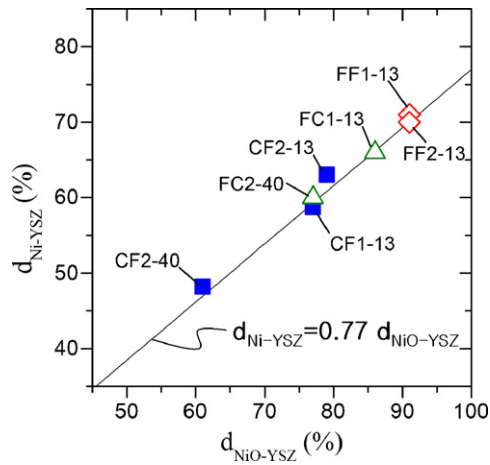
Fig. 3. The relative bulk density of NiO–YSZ sintered composites ($d_{NiO–YSZ}$) and Ni–YSZ cermets ($d_{Ni–YSZ}$) that were prepared by reducing the composites in H_2. Solid line represents the simulated values.

solid-state diffusion. Since the sintering between neighboring powders makes the microstructures dense, the inter-linkage of each phases would be a crucial factor for the densification of composites. As the coarse and fine powders, either NiO or YSZ, were mixed (FC- and CF-series), coarse particles were isolated by finer one and thus the densification by sintering was inhibited.

3.2. Electrical conductivity of Ni–YSZ cermet

The electrical conductivity of Ni–YSZ cermet under reducing atmosphere (10% H_2 balanced with Ar) was measured by four-probe dc method. Fig. 4 shows the typical temperature dependence of the electrical conductivity of Ni–YSZ cermets prepared by mixing with 13 or 40 vol% carbon black. All the samples showed the electrical conductivity of the range between 10^2 and 10^3 S cm^{-1}. The electrical conductivity was proportional to the reciprocal of absolute temperature, which is the typical behavior of metallic solids [12]. Considering relatively low ionic conductivity of 8YSZ ($\sim$0.2 S cm^{-1} at 1000 °C), the

high electrical conductivity and metallic behavior of the cermets imply that the electrical conduction of the cermets occurs through metallic Ni phase.

It was clearly found that the cermet prepared from fine NiO powder (FF1-40) showed one order of magnitude higher conductivity than those from coarse NiO powders (FC1-, FC2-, and FC3-40) when fine YSZ powder was commonly used. Higher sintered density of FF1-40 (86%) than the others (74–77%) may not simply the cause of such a significant increase in the electrical conductivity. It would rather be convincingly explained by percolation in a binary composite consisting of conductive and insulating phases [13]. In the view of percolation phenomenon, finer insulating particles are expected to surround coarser particles and inhibit the contact between conductive particles increasing the percolation threshold. As for FC specimens, coarse NiO particles appeared to be covered by fine YSZ particles in Figs. 1a and 2a. The isolated Ni grains after reduction would not contribute on the electrical conductivity of Ni–YSZ cermet. Fine NiO in FF1-40, however, was dispersed well with YSZ (Fig. 1b) and thus interconnected with each other after reduced to nickel particles. It is more interesting that CF1-13 composed of coarse YSZ and fine NiO powders showed higher electrical conductivity than FF1-40 despite its lower sintered density (79% of theoretical density) than FF1-40 (86%). CF2-13 having the lowest sintered density (70%) among the samples also showed higher electrical conductivity than FC-series.

For the more clarity, the electrical conductivities measured at 800 °C were plotted as a function of the relative sintered densities for all series of samples as shown in Fig. 5. NiO–YSZ composites showed different sintered density depending on the sinterability of starting powders and the amount of carbon black addition as described previously. The electrical conductivity values of CF1-13 and CF2-13, which have the relative sintered densities of 70 and 79%, respectively, were higher than those of FC specimens having similar or higher sintered density (74–85%). In addition, CF2-13, despite its lower sintered density, showed comparable electrical conductivity value to that of FF1-40. Itoh et al. has also reported that the addition of coarse YSZ powder increased the electrical conductivity of Ni–YSZ cermet [14].
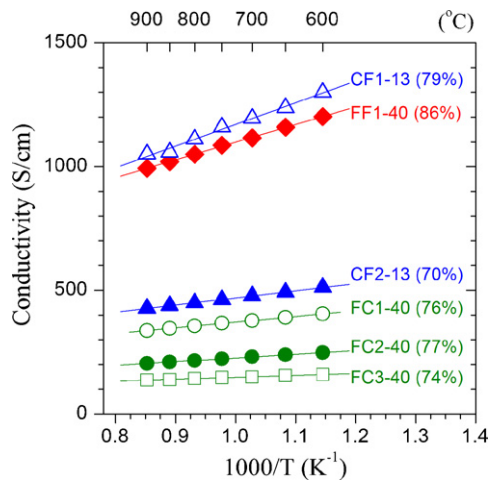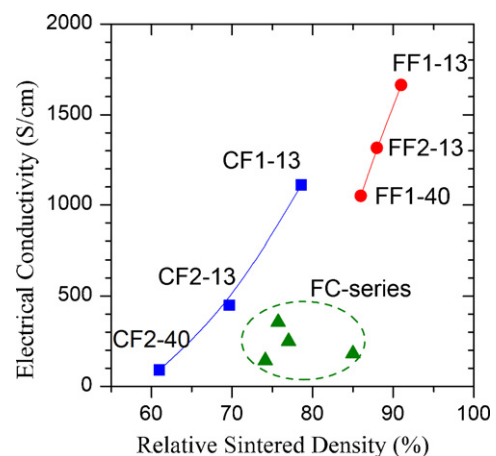

Fig. 4. Electrical conductivity of Ni–YSZ cermets as a function of temperature. Their relative sintered densities of NiO–YSZ composites are also presented in the blankets.

Fig. 5. Electrical conductivity of Ni–YSZ cermets prepared from a variety of powders plotted as a function of the relative sintered density of NiO–YSZ.

These results are consistent with the percolation theory that finer conductive particles reduce the percolation concentration [6]. Assuming nearly random distribution of two particles, fine NiO particles surrounding coarse YSZ particle in CF samples can be easily interconnected with each other during sintering and make Ni phase continuous through Ni–YSZ cermet after reducing as shown in Fig. 2c. As a result, the enhanced continuity of Ni in CF- and FF-series cause higher electrical conductivity than FC-series. Additionally the higher electrical conductivity of CF1-13 than FF1-40 indicates the better connectivity of Ni in the microstructure of CF1-13. Compared with FC-series samples, the use of fine NiO powder in FF-series also was effective to enhance the continuity of Ni particles.

The volume of insulating pores seems another crucial factor determining the electrical conductivity of anode cermet. Except for FC-series specimens with diverse sizes of Ni particle, the electrical conductivity of FF and CF-series proportionally increased with sintered density. It is clear that the higher sintered density enhanced the apparent electrical conductivity in FF and CF-series. This is not just because pore volumes geometrically reduce the effective current path, but because the increase of pores reduces the average number of contacts between individual particles and thus the percolation by Ni particles becomes poor. All the samples in this study had the same composition of Ni and YSZ, but the effective volumetric fraction of Ni in porous composites decreased with increasing porosity.

3.3. Fracture strength of Ni–YSZ cermet

Flexural strength of the Ni–YSZ cermets prepared with different starting powder is plotted as a function of porosity in Fig. 6. It is intuitively evident that the strength exponentially increased as the porosity of cermets decreased. The relationship between strength, σ, and porosity, p, can be described by:

$$\sigma = \sigma_o \exp(-bp), \tag{1}$$

where σ_o is the strength of the non-porous structure and b is a pre-exponential coefficient related with pore structure [15]. This relationship was derived from the assumption that the properties, such as elastic modulus, fracture toughness, electrical
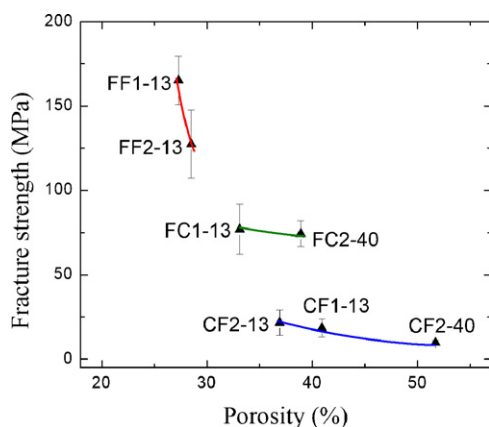

Fig. 6. Fracture strength of Ni–YSZ cermets as a function of porosity. Standard deviation is superimposed on each average value.

conductivity in addition to fracture strength, will be determined by minimum contact area of homogeneous spherical solid. The decrease of Young's modulus and shear modulus of NiO–YSZ with porosity has been reported earlier by Selçuk and Atkinson [16]. Radovic and Lara-Curzio [17] have successfully applied the equation to describe a strength–porosity relationship in Ni–YSZ system. However, if the properties of critical flaws or microstructure (such as particle size, shape, orientation, etc.) may affect factors such as stress concentration, more complex relationship should be suggested.

The data in Fig. 6 can be categorized apparently by three groups; FF, FC, and CF. The fracture strength of the specimens composed of fine-grained Ni and YSZ (FF group) is much higher than those of the other specimens, where one of the constituent phases, either Ni or YSZ, is coarse (FC or CF group). The high fracture strength over 100 MPa as for FF can be attributed to relatively low porosity (<30%) and small-sized pores. FF-series specimens had finer pores than FC- and CF-specimens as shown in Fig. 2, and thus the crack would propagate slowly along the small pores under mechanical stress.

On the other hand, strength of FC specimens is generally higher than those of CF1-13 and CF2-13 specimens despite of their similar porosities. In other words, coarse-grained YSZ significantly degraded the strength of the cermet compared with coarse-grained Ni. YSZ phase constitutes a framework of Ni–YSZ cermet, which determines the mechanical strength. All the cermets showed the typical fracture behavior of ceramics, of which strain–tress curves appeared linearly. As for the electrical conduction the percolation of Ni particles was the crucial factor and it was found that CF specimens showed much higher electrical conductivity than FC specimens in Figs. 4 and 5. As the fracture strength of cermets, however, would be mainly determined by the percolation of YSZ phase during sintering, CF specimens of which coarse YSZ grains were isolated by fine Ni particles (Fig. 2) showed three times lower fracture strength ∼25 MPa than FC specimens (∼75 MPa) composed of fine YSZ grains percolated better. Grahl-Madsen et al. fabricated NiO–YSZ anode support with coarse NiO and YSZ powders, and it was found that the mixing of fine YSZ powder enhanced the mechanical strength [18]. The enhanced mechanical strength can also be explained more clearly by the percolation of YSZ phase.

Interestingly, FF1-13 showed higher strength (165 MPa) than FF2-13 (127 MPa) in spite of their similar intergranular fracture mode and porosity after reduction. Although it is difficult to distinguish significant differences in microstructure, the distribution in size and shape of Ni particle seems to be heterogeneous for FF2-13, and which might cause a failure under relatively lower local stress from critical surface flaws. According to Inglis theory [19], if pore acts as a failure origin, a spherical shape of pore can relax the local stress at the tip as indicated in Eq. (2) because the local stress, σ_C, at the tip of an elliptical cavity is expressed as;

$$\sigma_C = \sigma_A[1 + 2(c/\rho)^{1/2}] \tag{2}$$

where σ_A is the applied stress, c the longer length of semi-axes, and ρ is the radius of curvature. Homogeneous distribution of

pore in FF1-13 specimen can be attributed to the high averaged value and small deviation in the strength.

4. Conclusions

The microstructure of Ni–YSZ cermets was modified by using commercial NiO and YSZ powders with different average particle sizes and by changing the amount of carbon black addition. The electrical and mechanical properties of the Ni–YSZ cermets were investigated and correlated with the microstructure including porosity, grain size and distribution of each phases. It was clearly found that the coarser particles were easily isolated by fine ones and the percolation of finer particles, either Ni or YSZ, during sintering strongly enhanced the electrical and mechanical performances, respectively. Coarse NiO powders with fine YSZ powder (FC specimens) made the Ni–YSZ cermets relatively resistive but the mechanical strength was good due to the percolated YSZ phase. On the contrary, Ni–YSZ cermets of coarse YSZ and fine NiO powders (CF specimens) showed high electrical conductivity and poor fracture strength. The use of fine NiO and fine YSZ powders (FF specimens) made fine microstructure with both phases percolated well and thus good electrical and mechanical properties.

Acknowledgements

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