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Morphological evolution of NiO-ScSZ composite in a high-temperature reducing atmosphere

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Abstract

The microstructural change in composite of nickel oxide and scandia-stabilized zirconia (NiO-ScSZ) under a reducing atmosphere was observed by scanning electron microscopy (SEM). The morphological transformation was noticeable after high-temperature treatment with the formation of two peculiar microstructures; *i.e.*, fibrous zirconia and metallic nickel with wrinkled surface. It was suggested that partial reduction of the nickel species dissolved in ScSZ lattice triggered the formation of these characteristic morphologies. The growth of fibrous zirconia appeared to be promoted via interfacial reaction between the metallic Ni particles and the zirconia phase. The agglomeration of metallic nickel proceeded by the reduction at high temperatures and then the surface was transformed to the wrinkled morphology. The unique wrinkled pattern was often observed for the large agglomerated nickel particles. This drastic change in Ni-ScSZ microstructure upon the high-temperature reduction degraded the electrochemical performance of solid oxide fuel cells.

Keywords: Ni-ScSZ; Reduction; Phase transition; Morphology; SEM

1. Introduction

Zirconia composite materials are currently attractive candidates in various applications. For example, zirconia-based oxides conductors have been employed extensively in oxygen sensors and solid oxide fuel cells (SOFCs) due to their prominent ionic conductivity and chemical stability under both reducing and oxidizing atmospheres at high temperatures.[1] In SOFC applications, the prerequisites of the basic requirements for anode materials are completed by the use of cermets, which is the mixture of ceramic and metal. The mixing of these two materials leads to an increase in the contact region between ionic- and electronic conductors, resulting in the expansion of the active reaction zone for the anode. Thus, the cermet microstructure with optimal distribution of the two components is desired in SOFCs. The Ni-oxide cermet systems, *i.e.*, nickel-yttria-stabilized zirconia (Ni-YSZ), nickel-scandia-stabilized zirconia (Ni-ScSZ), and nickel-samaria-doped ceria (Ni-SDC), are conventionally selected as anodes for the oxidation of various kinds of fuels.[2–4] Among the cermet anodes, Ni-ScSZ shows the superior and stable performance especially in the internal reforming operation with hydrocarbon fuels due to the excellent tolerance to carbon deposition originated from the high ionic conductivity of ScSZ.[5] Recently, we have reported the phase stability of 10 mol% Sc_2O_3-ZrO_2 (ScSZ) in the cermet of Ni-ScSZ subjected to heat treatments at high temperatures under reducing and oxidizing atmospheres.[6,7] It was clarified that the solid state reaction between NiO and ScSZ proceeded at high temperature in air, resulting in the phase transition from the rhombohedral to the cubic. Furthermore, the reversible phase transformation was observed (cubic → rhombohedral) after the high-temperature reduction treatment depending on the preparation methods of the cermets. The cermet anode may be continuously exposed to such extreme reducing conditions in the combined system integrated with gas turbine. Thus, we have to well consider the physical and chemical stability of the composite anode in the operating environments. The change in morphologies and microstructures of the anode under reducing conditions

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and subsequent operation also affects the cell performance.[8] Accordingly, it is of great importance to reveal the reduction behavior of NiO-ScSZ composite for the design of optimum anode.

In this study, therefore, we investigated the morphological change in NiO-ScSZ under a reducing atmosphere. The effects of the sample preparation methods, the contents of NiO in the starting materials, and the reduction temperatures were evaluated to clarify the process of morphological and microstructural changes upon reduction. The samples were characterized by scanning electron microscopy (SEM) with elemental analysis and X-ray diffraction (XRD) before and after reduction treatments. The effect of microstructural change on the electrochemical performance of a single cell with Ni-ScSZ anode after the high-temperature reduction treatment was evaluated.

2. Experimental

A composite material of NiO-ScSZ (10 mol% Sc_2O_3-ZrO_2) was prepared from the co-precipitation method (abbreviated as CP) as shown in the previous work.[6] The NiO contents in the composite were controlled to be 1 mol%, 50 wt.% and 80 wt.%. The metallic nitrates and NH_3 water were used as starting precursors and a precipitator, respectively. The aqueous nitrate solution was rapidly poured into 2 M NH_3 solution. The resultant suspension was aged at 80 °C and heated at 120 °C overnight. After drying, the powder was subsequently calcined at 1200 °C for 5 h. The composite of NiO-ScSZ was also prepared from the conventional powder mixing (PM) method. The commercial powders of NiO (Wako Pure Chemicals) and ScSZ (10 mol% Sc_2O_3-ZrO_2, Daiichi Kigenso Kagaku Kogyo) were ball-milled in dry condition overnight. The composite was subsequently calcined at 1200 °C for 5 h.

The samples from the CP and PM methods were heated again at 1200 °C for 5 h. The resultant powders were ground and isostatically pressed at 200 MPa into a disk substrate (*ca.* 5 mm in thickness, 10 mm in diameter). The dense substrates were fired at 1400 °C for 5 h in air. The NiO and ScSZ substrates were also prepared individually in the same manner for comparison. Scanning electron microscopy (SEM equipped with energy-dispersive X-ray spectroscopy (EDX, Oxford), NVision40, Carl Zeiss-SIINT) observation was conducted to analyze the changes in morphology and microstructure of NiO-ScSZ subjected to the reduction treatments at high temperature from 1000 °C to 1400 °C for 5 h in dry hydrogen. The crystalline structure of the powders was determined by X-ray diffraction (XRD, Rigaku, Ultima IV X-Ray diifractrometer) using Cu K_α radiation.

The electrochemical performance of a single cell with the Ni-ScSZ anode and Pt cathode was studied at 1000 °C. The composite powder of NiO-ScSZ (50 wt.% NiO) was prepared by the CP method. The anode slurry was screen-printed on one face of the YSZ disk electrolyte (8 mol% Y_2O_3-ZrO_2, 500 μm-thick, Tosoh) and subsequently fired at 1200 °C in air for 5 h. Platinum paste was applied as a cathode on the other face of the disk and then fired at 1200 °C in air for 5 h. Prior to the test, the cell was subjected to the reduction treatment in dry hydrogen at 1400 °C for 5 h. The fabricated cell was attached to an alumina tube and sealed with a glass o-ring. Platinum wire was attached as a reference electrode to surround the side edge of YSZ disk, fixed with Pt paste, and fired at 900 °C for 2 h in air. The electrochemical properties were monitored by a potentio/galvanostat (Solartron Analytical 1470E) and a frequency response analyzer (Solartron Analytical 1400) by supplying 97% H_2-3% H_2O and oxygen to the anode and cathode, respectively, at a flow rate of 100 ml/min. Impedance spectra were analyzed in a frequency range of 0.1 Hz to 1 MHz with a voltage amplitude of 10 mV.

3. Results and Discussion

3.1. The influence of reduction temperature

The composite of NiO-ScSZ with 50 wt.% of NiO was selected to evaluate the influence of reduction temperatures between 1000 °C to 1400 °C on the morphological transformation. The NiO-ScSZ composite powder was prepared from the CP method. Fig. 1 shows the microstructure of the pelletized Ni-ScSZ cermets before and after the reduction treatments. For the as-prepared composite, the formation of terrace texture was observed on the surface of NiO, which was confirmed by EDX analysis. SEM images of composites after the reduction treatment indicated the change in the microstructure. The particles and pores were uniformly distributed after the reduction at 1000 °C. In general, the reduction of NiO to metallic Ni leads to the volume change in the composite. The Ni species appeared to move to the pellet surface with agglomeration during the reduction at 1200 °C as shown in Fig. 1(c).

The sintering of metallic nickel remarkably proceeded after reduction at and above 1300 °C. It was obviously found that most of the Ni particles tended to grow to large agglomerates with the size of more than 1 μm. With an increase in reduction temperature to 1350 °C, the microstructure of Ni-ScSZ exhibited peculiar particles with wrinkled surface as shown in Fig. 1(e). The elemental analysis by EDX indicated that the particle with the wrinkled surface was attributed to the metallic Ni. Interestingly, the morphological transformation of nickel particles from smooth to the wrinkled surface was self-initiated under a reducing atmosphere at 1350 °C because reduction of ScSZ did not proceed thermodynamically at 1000–1400 °C. Some small Ni particles with smooth surface were also observed on the surface of zirconia as shown in Fig. 1(f). After reduction at 1400 °C, the drastic microstructural change was observed (see Fig. 1(g) and (h)). Note that plenty of small particles connected with fibers were formed. The elemental analysis revealed that the fiber consisted of zirconia and the tiny spherical particles corresponded to metallic Ni. Recently, the morphological change of the zirconia mixtures by applying high voltage (10–30 kV) to the precursors has been studied[9–18]; the zirconia composite with fibrous structure with smooth surface was formed after heat-treatment at high temperatures (800–1500 °C). In this study, however, the fibrous zirconia was successfully self-assembled without the high voltage treatment. The size of small Ni particles connected with zirconia fiber was comparable to that of the spherical particles observed in Fig. 1(f). Such tiny particles of spherical Ni were

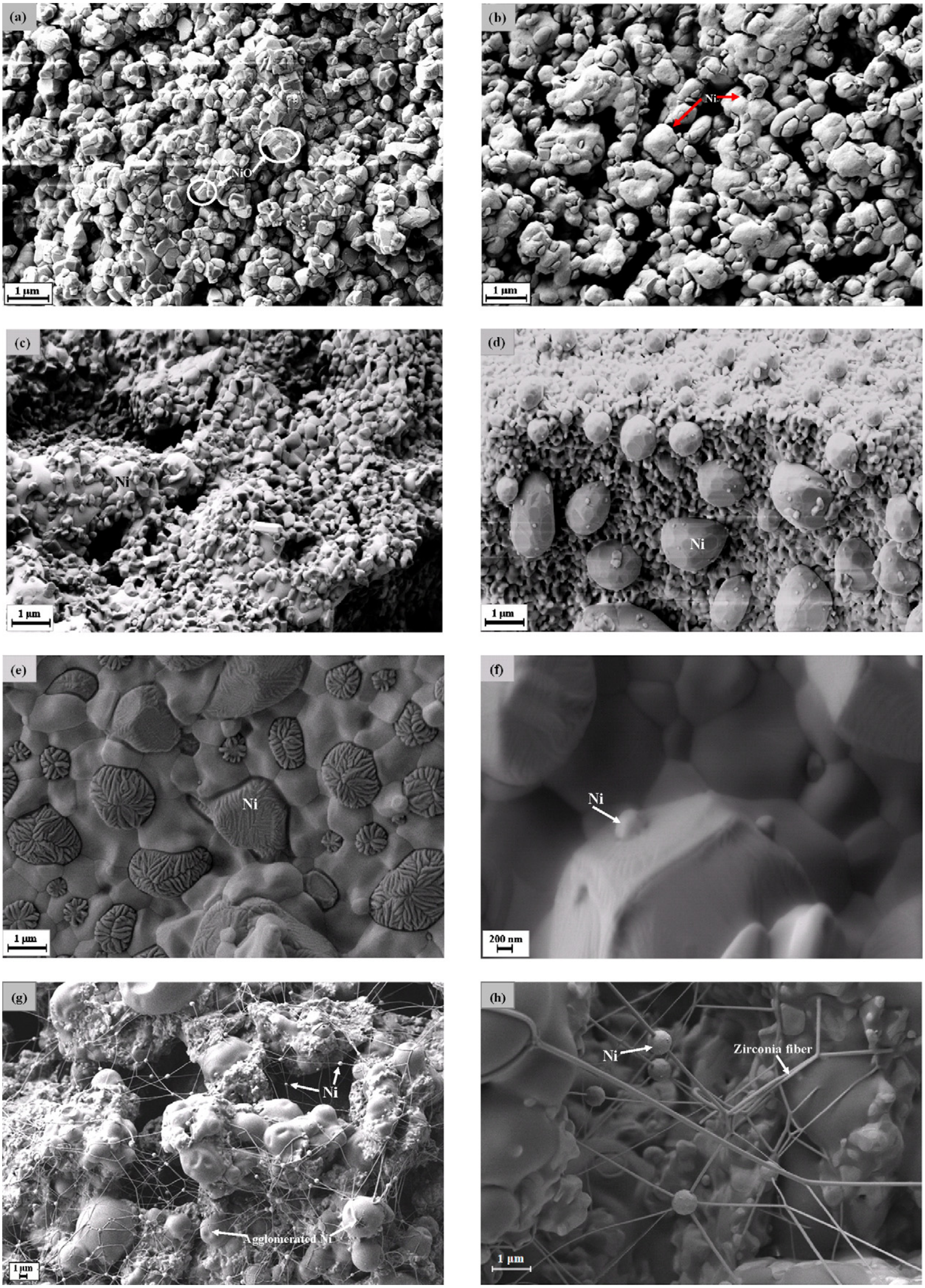

Fig. 1. SEM images of the NiO-ScSZ (50 wt.% of NiO, CP method) microstructure (a) before reduction and (b–h) after reduction in dry hydrogen at (b) 1000 °C, (c) 1200 °C, (d) 1300 °C, (e, f) 1350 °C, and (g, h) 1400 °C for 5 h.

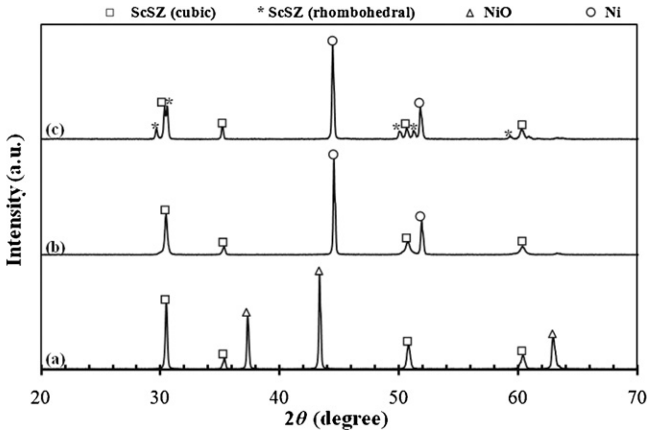

Fig. 2. XRD patterns of the NiO-ScSZ composite (50 wt.% of NiO, CP method) (a) calcined at 1200 °C in air, and (b, c) after subsequent reduction in dry hydrogen at (b) 1000 °C and (c) 1400 °C for 5 h.

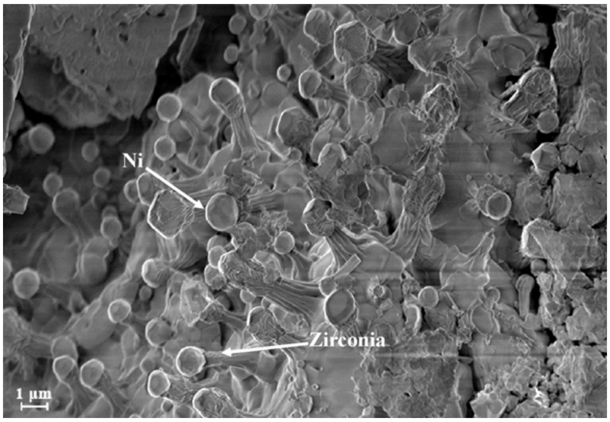

Fig. 3. SEM image of the Ni-ScSZ (1 mol% of NiO, CP method) microstructure after reduction in dry hydrogen at 1400 °C for 5 h.

separately formed without agglomeration. The dissolution of NiO into ScSZ and subsequent phase separation of Ni from the solid solution should be responsible for the formation of these small particles.

The crystalline structure of the NiO-ScSZ powder with 50 wt% of NiO before and after reduction treatments is illustrated in Fig. 2. As reported previously, the solid state reaction was promoted during firing at high temperatures leading to the dissolution of some portions of nickel species into the rhombohedral phase of ScSZ (10 mol% Sc_2O_3-ZrO_2) lattice.[6] The dissolution of nickel species results in the stabilization of cubic phase of ScSZ. After calcination at 1200 °C in air and subsequent reduction at 1000 °C for 5 h, accordingly, the XRD patterns clearly showed the cubic phase of ScSZ. In contrast, the partial transition to the rhombohedral phase of ScSZ proceeded after reduction at 1400 °C. These results indicated that the reduction of the dissolved Ni cations in the ScSZ lattice was preferentially induced at 1400 °C, resulting in the formation of nickel deposites on zirconia surface accompanied with the phase transition. These deposited particles appear to play an important role for the formation of zirconia fibrous network. Consequently, the microstructural evolution of Ni-ScSZ could be remarkably enhanced by the reduction treatment at extremely high temperatures.

3.2. *The influence of the NiO content*

The composite of NiO (1 mol%)-ScSZ prepared by the CP method exhibited the morphological change after reduction at 1400 °C for 5 h. Fig. 3 shows the SEM image of the Ni-ScSZ cermet. The sample exhibited the elongated rod-shaped structure with a spherical particle on its tip, which was analogous to the morphology of mushroom. The textures elongated from the surface and the spherical particles were attributed to zirconia and metallic Ni, respectively, by EDX analysis. The formation of elongated rods of zirconia will correspond to the initial evolution of fibrous network observed in Fig. 1(g) and (h). The solubility limit of NiO in ScSZ and YSZ is reported to be 1 and 2 mol%, respectively.[19,20] Thus, a portion of the NiO species was dissolved into the ScSZ lattice during the calcination at 1200 °C under an oxidizing atmosphere. This was confirmed by the crystalline structure of NiO-ScSZ as the cubic phase stabilization in ScSZ (see Fig. 2). After reduction at 1400 °C, the Ni species in the zirconia lattice was readily reduced to form spherical particles as shown in Fig. 3. As mentioned above, these metallic Ni particles will significantly affect to the formation of zirconia fiber. Considering the existence of zirconia fibrous network in Ni-ScSZ with 50 wt.% of NiO, the amount of metallic Ni may have a considerable impact on the growth of the fibrous zirconia. Some agglomerated particles of metallic nickels were also observed (data not shown) for the sample reduced at 1400 °C. The coarsening of Ni particles involved the mass transfer process initiated from the smaller to the larger Ni particles leading to the grain growth by the Ostwald ripening to reduce the surface energy of the system.[21,22]

3.3. *The influence of preparation method*

To investigate the influence of preparation methods, the composite of NiO-ScSZ was also prepared by the powder mixing (PM) method. Fig. 4 shows the microstructure of Ni-ScSZ after reduction at 1400 °C for 5 h. The formation of both large particles with wrinkled surface and zirconia fiber was confirmed regardless the preparation methods. The zirconia fibers attached with small particles were formed upon the reduction treatment at high temperatures. Because of the similarity in the microstructure after reduction for both samples prepared by the CP and PM methods, it could be accepted that the preparation method has little influence on the formation of these characteristic structures. Cui et al.[11] reported the fabrication of ZrC nanofibrous structure by annealing a mixture of zirconia and carbonaceous precursors; the formation of ZrC fibers was initiated from the interfacial reaction between zirconia and carbonaceous species at extremely high temperatures (more than 1500 °C). Thus, in this study, the formation of fibrous zirconia could be also initiated by the interfacial reaction between zirconia and metallic Ni particles in small size at the reduction temperature of 1400 °C. At the same time, some Ni particles were also agglomerated along with the microstructural change

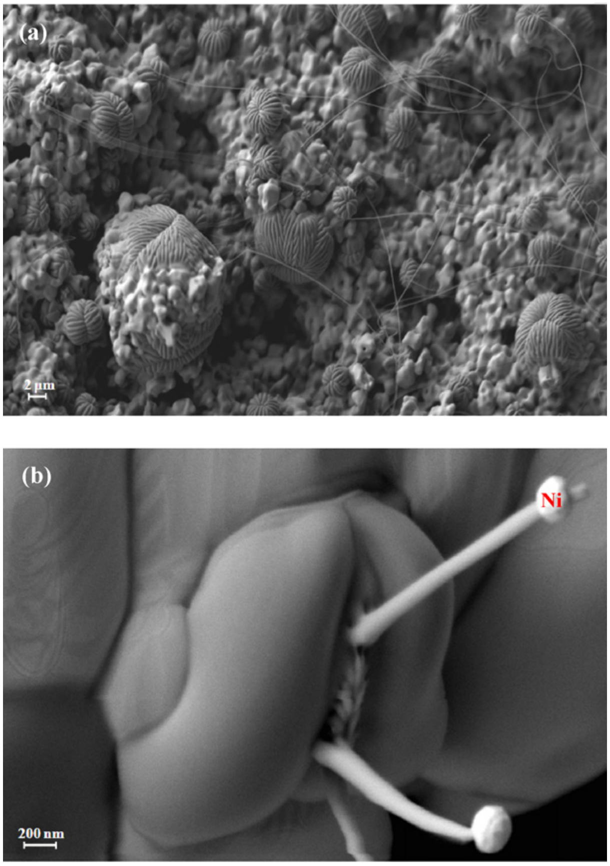

Fig. 4. SEM images of the Ni-ScSZ (50 wt.% of NiO, PM method) microstructure after reduction in dry hydrogen at 1400 °C for 5 h.

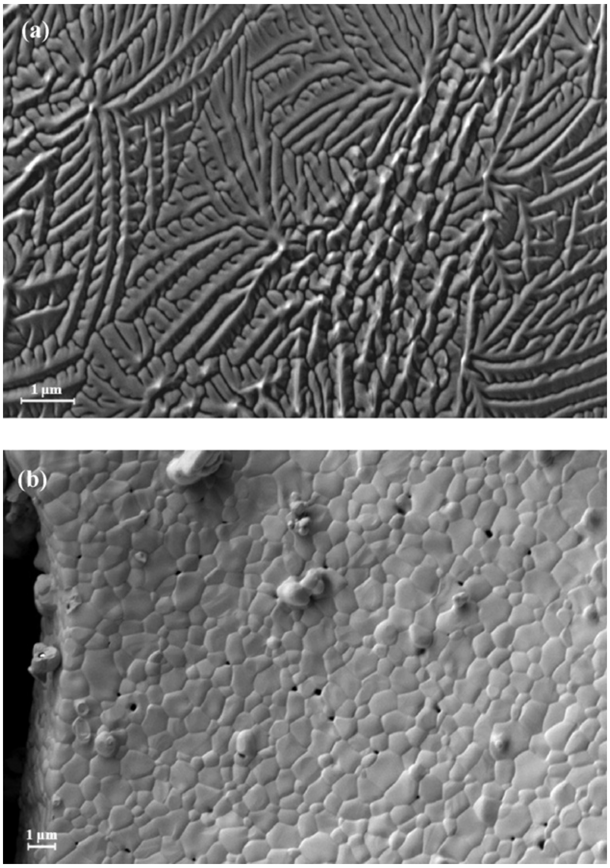

Fig. 5. SEM images of the surface of (a) NiO and (b) ScSZ after reduction in dry hydrogen at 1400 °C for 5 h.

in the surface morphology to the wrinkled shape as shown in Fig. 4(a). Laguna-Bercero et al.[21] have reported the reduction of interfacial energy between Ni and zirconia support by the coarsening of Ni particles. Therefore, these large Ni particles will not contribute to the formation of the fiber structure due to the insufficient energy to promote the interfacial reaction with zirconia.

In order to obtain more information about the impact of each component on the microstructural change upon the reduction, the substrates of NiO and ScSZ were separately prepared and reduced at 1400 °C for 5 h. The surface morphologies of Ni and ScSZ substrates after reduction are shown in Fig. 5(a) and (b), respectively. Metallic Ni will be readily sintered in this condition because the reduction temperature is close to the melting point (*ca.* 1450 °C). The wrinkled surface was clearly observed in the NiO substrate after reduction. In contrast, no significant change in the morphology of the ScSZ substrate was found. It was confirmed by the thermodynamic equilibrium calculation that ScSZ is not reduced at 1400 °C. Thus, the reduction of Ni species in the zirconia lattice triggers the microstructural change in the NiO-ScSZ composite.

Based on the morphological observations, the prospective mechanism for the growth process of wrinkled surface and fibrous structures is suggested as follows. The composite of NiO-ScSZ was initially prepared and the solid state reaction proceeded by the calcination at high temperatures in air. Such high-temperature treatment resulted in the dissolution of NiO species in the ScSZ structure.[19] The microstructural change was initiated by exposing in the reducing atmosphere at high temperatures. The reduction of dissolved Ni species gave rise to the formation of small metallic Ni particles, which promoted the growth of the zirconia fibers via interfacial reaction. On the other hand, the diffusion of Ni species on the surface induced the agglomeration accompanied with the change from the smooth surface to the wrinkled one.

The electrochemical property of the single cell with the Ni-ScSZ anode was investigated at 1000 °C. *I-V* and *I-P* characteristics of the single cells with different reduction treatment are displayed in Fig. 6. The performance was noticeably low as compared with the cell with the Ni-ScSZ anode after reduction treatment at 1000 °C in previous study.[6] The maximum power density was only *ca.* 0.8 mW cm^{-2} in hydrogen fuel at 1000 °C. However, without the reduction treatment at 1400 °C, the previous study has reported the maximum power density *ca.* 420 mW cm^{-2} in the same operating conditions (see Fig. 6 (b)). The inferior performance was confirmed due to a result of the morphological change of Ni-ScSZ after reduction treatment at 1400 °C. Fig. 7 shows the impedance spectra of the corresponding cells in Fig. 6 measured in the open-circuit condition. Although in the previous study the polarization resistance of Ni-ScSZ anode operated at 1000 °C was *ca.* 0.35 Ω cm^2, the resistance drastically increased to *ca.* 440 Ω cm^2 in association

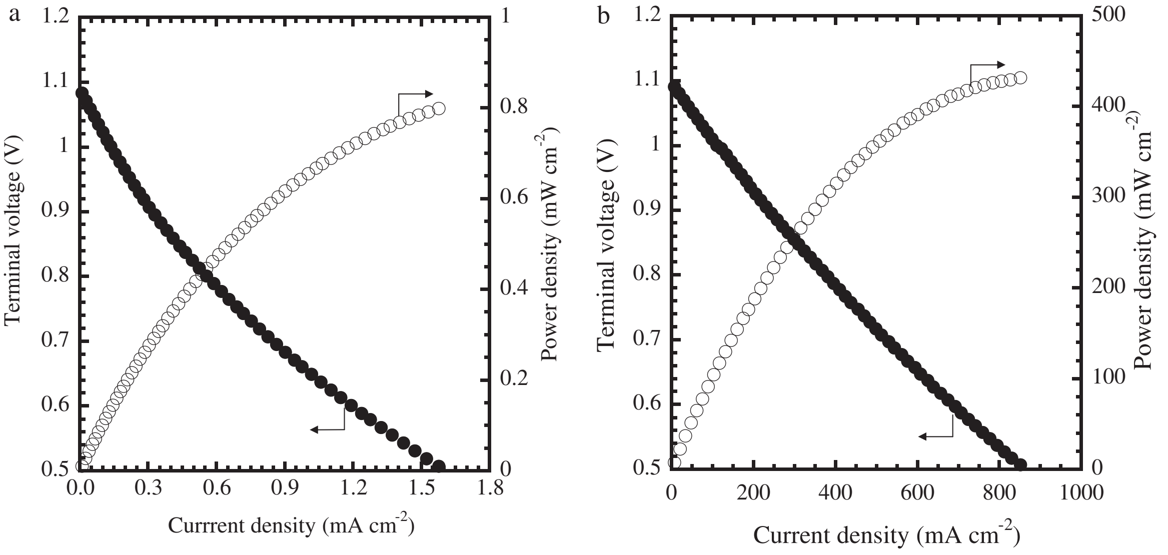

Fig. 6. *I-V* and *I-P* characteristics of a single cell with Ni-ScSZ anode at 1000 °C in 97% H_2–3% H_2O. The cell was reduced in dry hydrogen at (a) 1400 °C or (b) 1000 °C[6] for 5 h prior to the test. Cell configurations; Ni-ScSZ|YSZ|Pt and Ni-ScSZ|YSZ|LSM.[6]

with the microstructural change of Ni-ScSZ anode after reduction pretreatment at 1400 °C. The distinct change observed by SEM images revealed the detrimental sintering of the metallic Ni, which was ascribed to a main reason for the abnormally low performance. Accordingly, the high-temperature treatment in a reducing atmosphere developed the drastic change in microstructure of the Ni-ScSZ cermets which was ineffective for SOFC applications.

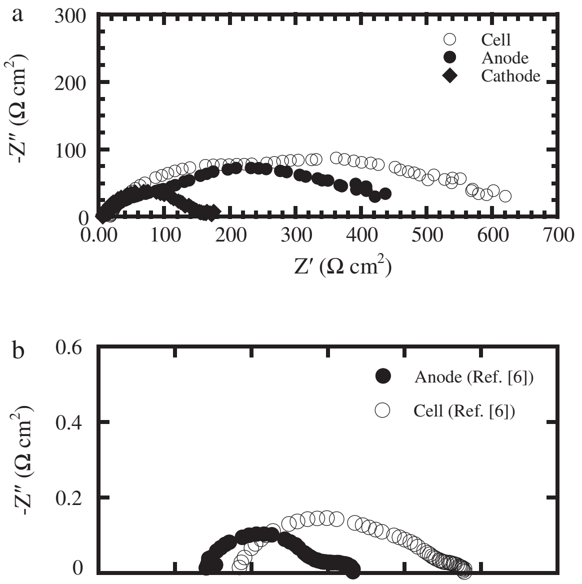

Fig. 7. Impedance spectra of a single cell under the open-circuit condition at 1000 °C corresponding to Fig. 6.

4. Conclusions

The influence of reduction treatments on the morphology of NiO-ScSZ composite was investigated. Spherical shape of small nickel particles with the elongated rod-liked texture of zirconia was observed in the NiO-ScSZ composite with 1 mol% of NiO content after reduction at 1400 °C for 5 h. The formation of zirconia fiber was clearly observed after reduction of the sample with 50 wt% of NiO at 1400 °C. The phase transition of cermets observed by XRD measurement indicated that nickel oxide species were dissolved in the ScSZ phase during the calcination in air, and then metallic particles of nickel was deposited during the reduction at 1400 °C. It was noted that the deposited Ni particles catalytically promote the growth of fibrous zirconia by the interfacial reaction between zirconia and Ni. At the same time, some Ni species were agglomerated to form large particles accompanied with the change of the exposed surface to the wrinkled surface. Regarding to the evidently transformed microstructure of Ni-ScSZ cermet, the electrochemical performance of the single cell with Ni-ScSZ anode was deteriorated. Accordingly, this study revealed a key information of the remarkable change in microstructure in the reducing atmosphere, which strongly affected the electrochemical performance as in the SOFC applications.

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