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Microstructure and Electrical Conductivity of Ni-YSZ Cermets Prepared by Combustion Synthesis Method

Tiesong Lin[1], Dechang Jia[1] and Kening Sun[2]

[1] Institute for Advanced Ceramics, Harbin Institute of Technology, Harbin 150001, China

[2] Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, China

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Abstract. Ni-YSZ cermets were prepared by combustion synthesis of $Y(NO_3)_3$, $Zr(NO_3)_4$, $Ni(NO_3)_2$ and urea followed by hydrogen reduction at 800°C. The microstructure and electrical conductivity of Ni-YSZ cermets were investigated as contrasted to those of the cermets with the same Ni contents prepared by mechanically mixing method. The cermets prepared by combustion synthesis method had better homogeneity of Ni distributed in YSZ than those prepared by mechanically mixed method; thus, both Ni and YSZ phases formed, to a certain extent, a continuous network structure. The electrical conductivity of the cermets prepared by combustion synthesis method was always better than that obtained with the samples prepared by mechanically mixed method.

Introduction

Due to its high efficiency, environmentally friendly nature, fuel adaptability and high reliability, solid oxide fuel cell (SOFC) is considered to be one of the most promising energy converters in the 21st century [1,2]. At present, Ni-8mol% yttria stabilized zirconia (Ni-YSZ) cermet is the most widely adopted materials for SOFC anodes due to their excellent electrocatalytic property and low price [3]. In previous studies, Ni-YSZ cermet was usually manufactured by mechanically mixed method. NiO and YSZ powders were mechanically mixed and then sintered to form NiO-YSZ composite ceramics. The NiO is then reduced to in situ Ni metal with hydrogen. Obviously, mechanically mixed method is simple, but it is very difficult to guarantee a very uniform distribution of Ni particles in the YSZ matrix. This may result in low-level three-phase boundaries (TPB) among electrolyte, electrode and gas phase, which can act as electrochemically active sites for electrode reactions. In addition, the growth up of the Ni particles will reduce the area of TPB during thermal treatment and subsequent cell operation [4]. Therefore, it is very important to select a simple and effective method to prepare fine and homogeneous starting powders for high electrode performance and stability [5].

In this paper, Ni-YSZ was prepared by combustion synthesis of nitrate and urea followed by hydrogen reduction. By controlling Ni contents, Ni-YSZ with different microstructures was obtained. The microstructure and electrical conductivity of Ni-YSZ were characterized as contrasted to those of the cermets with the same Ni contents prepared by traditional mechanically mixing method.

Experiments

NiO-YSZ powders were prepared by combustion synthesis method. $Ni(NO_3)_2{\cdot}6H_2O$, $Zr(NO_3)_4{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$, and urea were used as starting materials. According to the concepts in propellant chemistry, two idealized reactions during the synthesis can be written as follows [6]:

$$16Y(NO_3)_3+0.92Zr(NO_3)_4+5CO(NH_2)_2=0.08Y_2O_3+0.92ZrO_2+5CO_2+10H_2O+7.08N_2 \quad (1)$$

$$6Ni(NO_3)_2+10CO(NH_2)_2=6NiO+10CO_2+20H_2O+16N_2. \quad (2)$$

Nitrates and urea with stoichiometric proportions were first mixed together in an Al_2O_3 crucible, and then dissolved with de-ionized-water. The solution was kept over a water bath at 60°C until a bright green gel formed. The crucible was then introduced into a muffle furnace pre-heated at 350°C. Combustion reaction took place immediately, and a large amount of heat and yellow brown gas were emitted out. The flame was sustained for several seconds, and subsequently foamy dark green powders were yielded. In this paper, the urea used in the reaction mixtures is nearly 1.5 times as much as theoretical value according to Eqs. (1) and (2).

To prepare Ni-YSZ, the powders of NiO-YSZ obtained were compacted into pellets and then sintered at 1400°C in air for 2h, and finally reduced under flowing hydrogen at 800°C for 4h. Ni-YSZ with Ni/YSZ mol ratios of 2/1, 5/2 and 3/1were prepared, respectively. For comparison, Ni-YSZ were also prepared by mechanically mixed method under the identical conditions.

Microstructure of Ni-YSZ was studied using a scanning electron microscopy (SEM). Electrical conductivity was measured with DC four-probe technique as a function of temperature from 100 to 850°C in a reductive atmosphere.

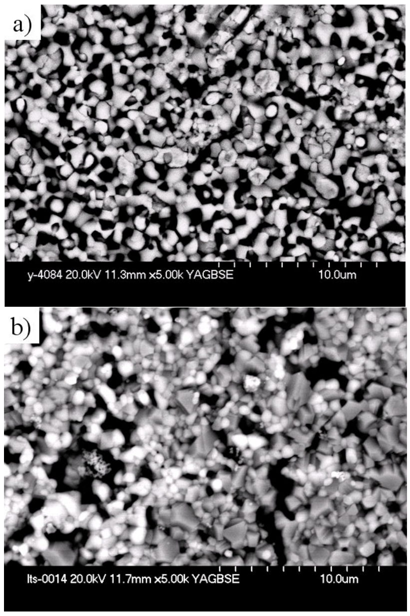

Fig.1 SEM micrographs of Ni-YSZ cermets prepared. a) by combustion synthesis method; b) by mechanically mixed method

Results and Discussion

Microstructure. SEM micrographs of Ni-YSZ cermets are shown in Fig.1. The microstructure of Ni-YSZ prepared by combustion synthesis method (Fig. 1(a)) exhibited good homogeneity. The particles were relatively spherical. The particle size distribution was fairly narrow with an average particle size in the range of 0.5~1μm. Clearly, fine Ni particles were distributed uniformly with fine pores surrounding them. For Ni-YSZ cermets prepared by mechanically mixed method, the particles exhibit a broad distribution in sizes and partial agglomeration (Fig. 1(b)). Combustion synthesis method used in the present study may assure more homogeneous distribution of Ni in YSZ matrix and more reasonable microstructure.

As SOFC works in high temperature environment, coarsening of Ni particles usually takes place [7]. Although the loss of the percolation among metallic grains with time and thus the decrease of the TPB cannot be avoided completely, it can be reduced substantially by yielding well-mixed narrow sized particles to control microstructure of the cermets.

Fig.2 shows the SEM photographs of Ni-YSZ prepared by combustion synthesis method sintered at 1400°C for 2h and reduced at 800°C in H_2. Dark areas in the micrographs correspond to pores; while gray and white areas are Ni and YSZ, respectively. The samples with Ni/YSZ ratio of 2/1 and 5/2 as shown in Fig.2 (a), (b) clearly show that Ni particles had embedded into YSZ phase, and YSZ phase had formed a continuous network structure. The conductivities of these two samples are $138 S \cdot cm^{-1}$ and $840 S \cdot cm^{-1}$ at 800°C, respectively (Fig. 3), which are much larger than that of YSZ (the electrical conductivity of YSZ was ~ $0.01 S \cdot cm^{-1}$ at 800°C [8]). This indicates that Ni phase was the main path for conduction. In other words, the conduction of Ni- YSZ was dominated by the motion of electrons, and Ni phase had also formed, to a certain extent, a continuous network structure. So, both Ni and YSZ formed continuous network structures, respectively. These structures may help to extend

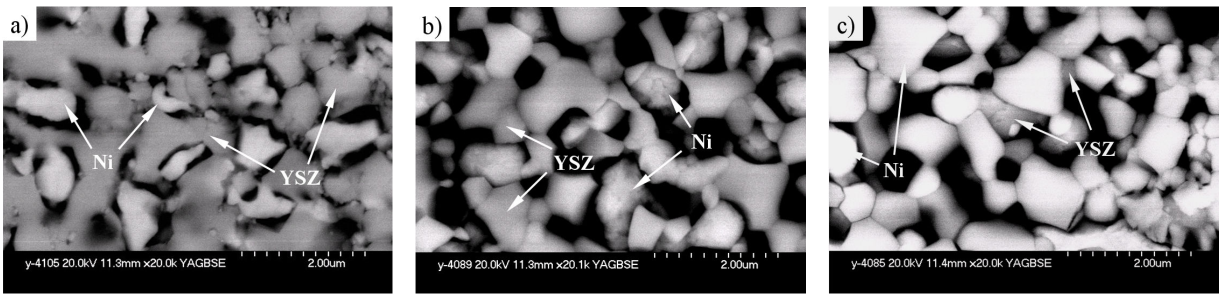

Fig.2 SEM micrographs of Ni-YSZ sintered at 1400°C and after reduction. a) Ni/YSZ=2/1; b) Ni/YSZ=5/2; c) Ni/YSZ=3/1

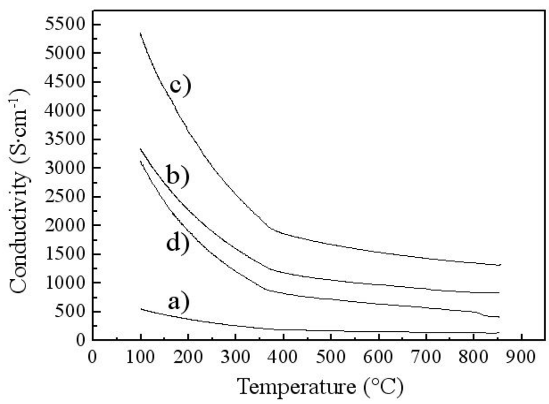

Fig.3 Electrical conductivity vs. temperature of Ni-YSZ prepared by combustion synthesis method. a) Ni/YSZ=2/1; b) Ni/YSZ=5/2; c) Ni/YSZ=3/1; by mechanically mixed method d) Ni/YSZ=5/2

the effective TPB into the anode layer, to prevent coarsening of Ni particle during thermal treatment and subsequent cell operation and to improve stability. With the increase of Ni contents, continuous network structure of YSZ was destroyed and the electrical conductivity of the sample increased (the electrical conductivity of cermet with Ni/YSZ ratio of 3/1was 1353S·cm^{-1} at 800°C as shown in Fig.2(c)).

Electrical Conductivity. From Fig. 3, the electrical conductivity of samples with different nickel contents differed significantly from each other, but they decreased with the increase of temperatures. This is consistent with that the motions of electrons decreased with increase of temperature. This confirmed that the main path of conduction is through Ni phase, and Ni phase had formed continuous networks as YSZ phase did.

Electrical conductivity of the cermets with a Ni/YSZ ratio of 5/2 prepared by different methods was compared. The electrical conductivity of the cermet prepared by combustion synthesis method was always better than that of the samples prepared by mechanically mixed method. The former was nearly two times as high as that of the latter at 800°C. The comparisons between the samples with other Ni/YSZ composition ratios prepared by these two methods were similar to the results as the above mentioned. As contrasted to mechanically mixed method, combustion synthesis method can assure more homogenous distribution of Ni in mixed NiO-YSZ powders and subsequently in the Ni-YSZ cermets, which is helpful for Ni particles to contact each other, and form a continuous and well-developed network, to improve electrical conductivity.

Conclusions

The combustion synthesis method is attractive for the preparation of Ni-YSZ cermets for SOFC. It enables mixing of precursors in the starting solution, resulting in a distribution of Ni particles in YSZ phase with a high degree of homogeneity. The microstructure of Ni-YSZ cermets reveals that both Ni and YSZ phases may form, respectively, to a certain extent, a continuous network structure with appropriate Ni contents. The electrical conductivity of the cermets is much better than that of the cermets prepared by mechanically mixing method in the temperature range of 100 to 850°C.

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