Effect of water vapor on static fatigue behavior of a nickel/yttria-stabilized zirconia composite

Tsuneaki MATSUDAIRA[†], Byung-Koog JANG^{*}, Sun-Dong KIM^{**} and Sang-Kuk WOO^{**}

Japan Fine Ceramics Center, Nagoya 456–8587, Japan

^{*}National Institute for Materials Science, Tsukuba, Ibaraki 305–0044, Japan

^{**}Korea Institute of Energy Research, Daejeon 305–343, Republic of Korea

The effect of water vapor on the mechanical properties of a porous nickel/yttria-stabilized zirconia (Ni–YSZ) composite (volume ratio of Ni:YSZ = 40:60) was evaluated at 850°C, a typical operating temperature of a reversible solid oxide cell. Both the flexural strength and static fatigue limit of Ni–YSZ obtained from the static fatigue lifetime under a wet atmosphere (containing 4% H₂O) were lower than those under a dry atmosphere. This can be explained by absorption of H₂O molecules into YSZ particles, resulting in accelerated crack growth. The fatigue limit of Ni–YSZ was confirmed to be extremely low, corresponding to almost one-third of the flexural strength.

©2017 The Ceramic Society of Japan. All rights reserved.

Key-words : Reversible solid oxide cell, Ni–YSZ, Water vapor, Flexural strength, Static fatigue, Fatigue limit

[Received December 1, 2016; Accepted February 16, 2017]

Hydrogen is one of the most abundant elements in nature, but obtaining it in its pure form requires separation from chemical compounds. Approximately 96% of hydrogen is produced from reforming reactions with natural gas, oil and coal gasification, with the remainder produced via renewable energy methods such as thermochemical, photoelectrochemical and biological water-splitting. Reforming methods are energy intensive and emit greenhouse gases, while renewable energy processes are costly and have too low efficiencies to satisfy demand.^{1),2)} A solid oxide electrolyzer is essentially a solid oxide fuel cell (SOFC) operating in reverse mode. As an alternative means of generating hydrogen they have attracted considerable attention due to their high efficiency (ca. 98%) when operated at high temperature (>650°C).³⁾ A reversible solid oxide cell (RSOC) combines fuel cell and electrolysis modes in a single device, so that in economic terms the payback period is less than 1 year. This is much shorter than other alternative hydrogen production methods, such as hybrid wind turbines (3–4 years) and hybrid photovoltaic panel systems (6–7 years).⁴⁾

The fuel electrodes of an RSOC, however, are subjected to high stress under redox conditions at high temperature, which can result in agglomeration of the electrode material, poor redox stability, and phase separation, thereby compromising the integrity of devices during operation. Thermal cycling and interphase reactions can also introduce large stresses. Consequently, the fatigue characteristics of the electrodes under various conditions are of principal interest for the development of robust RSOCs. In particular, the mechanical properties of porous nickel/yttria-stabilized zirconia (Ni–YSZ) composites are the focus of much attention because the majority of RSOCs under development employ an Ni–YSZ electrode support type structure. There have

been detailed studies on the elastic/plastic deformation of Ni–YSZ at SOFC operation temperatures under dry reducing atmospheres.^{5)–7)} However, there have been no studies on the effect of water vapor on the mechanical properties of Ni–YSZ, even though Ni–YSZ is exposed to wet atmospheres when used in SOFCs.

In this study, the effect of water vapor on the flexural strength and static fatigue lifetime of an Ni–YSZ composite (volume ratio of Ni:YSZ = 40:60) was evaluated at a temperature of 850°C. Previous work indicated that this volume ratio provides a suitable balance between good electrical conductivity and mechanical strength,⁸⁾ but the durability (and hence lifetime) of the fuel electrode under wet conditions was not examined. A test temperature at the higher end of RSOC operating temperatures was chosen for this study both to subject the system to the harshest conditions likely to be encountered in practice and to accelerate the degradation process so that any changes would be discernible after a short amount of time.

Flat-tubular supports were used because of their short current paths and ease of cell stacking. Flat-tubular YSZ composites containing nickel oxide (NiO) were prepared for mechanical characterization by an extrusion method described in detail elsewhere.⁸⁾ The raw materials for the support were NiO (04PB, Kojundo, Japan), YSZ (8 mol % Y₂O₃–ZrO₂; TZ-8Y, Tosoh, 100% cubic phase⁹⁾) and carbon black powder (L30, LG Carbon, South Korea).

The powders were mixed with NiO/YSZ ratios of 45/55 wt % in ethanol with a cellulose-type binder (YB-132A, Yuken Industry Co. Ltd., Japan) for 48 h, and then dried at 70°C. The mixing/kneading process was continued with an appropriate amount of the mixture and aqueous solvent, and the plastic mass was then aged overnight. Pre-extrusion and mixing in a vacuum mixing chamber were carried out three times to obtain a feedstock with high homogeneity. Flat tubes were then extruded continuously through a twin-screw extruder at room temperature. Each tube was dried at 120°C for 3 h after cutting to the desired length. The flat tubes were then sintered at 1400°C for 3 h

[†] Corresponding author: T. Matsudaira; E-mail: matsudaira@jfcc.or.jp

[‡] Publication of this international collaborative article is supported by JSPS Grants-in-Aid for Scientific Research (KAKENHI), Grant Number 252016

Fig. 1. Schematic diagram of the three-point bending jig and specimen.

followed by reduction at 900°C for 12 h in 50% H₂/Ar gas. Porous Ni-YSZ sintered bodies (volume ratio of Ni:YSZ = 40:60) were obtained by this reduction treatment. The densities and porosities of the sintered bodies were 4.8 g/cm³ and 30%, respectively. Bar-shaped specimens with dimensions of 3.0 × 3.0 × 30 mm³ were cut from the sintered bodies.

Three-point bending tests and static fatigue tests were conducted at 850°C. **Figure 1** shows a schematic diagram of the three-point bending jig and specimen. Ar-4% H₂ was employed for the dry atmosphere, and the same gas with P_{H₂O} maintained at around 4 × 10³ Pa by bubbling it through distilled water at 35°C was used for the wet atmosphere. The dry or wet gas was blown against the center of the side of the tensile surface¹⁰⁾ to prevent the oxidation of Ni in the specimen and to evaluate the effect of water vapor. Specimens were heated to 850°C at a heating rate of 5°C/min and held at that temperature for 15 min, after which three-point bending tests or static fatigue tests were performed. The gas flow rate was 0.3 L/min at room temperature, which became 1.1 L/min at 850°C due to expansion of the gases. The oxygen partial pressures of the gases for dry and wet atmospheres were measured using a zirconia sensor to be 10⁻¹⁸ and 10⁻¹² Pa, respectively. The oxygen partial pressure that corresponds to the phase boundary between Ni and NiO is estimated from thermodynamics to be 10⁻⁸ Pa. Therefore, static fatigue testing could be performed at 850°C for both dry and wet atmospheres without oxidation of the Ni in the stress applied region of the specimens.

Three-point bending tests were performed using a span of 16 mm at a constant cross-head speed of 0.5 mm/min. Static fatigue tests were performed under constant load at 850°C for 10⁵ s. Three specimens were tested under each condition for the three-point bending tests and static fatigue tests. In addition, the fatigue limit, where the maximum stress corresponds to no strength degradation during the static fatigue tests, was statistically determined using the residual strength and flexural strength^{11)–15)} measured at 850°C under a reducing atmosphere (Ar-4% H₂) to prevent the oxidation of Ni. Fracture surfaces of the specimens that failed during the static fatigue tests were observed using scanning electron microscopy (SEM).

Figure 2 shows typical load-displacement curves for the three-point bending tests. Both curves under dry and wet atmospheres show that the load increased linearly above about 0.05 mm, and then suddenly decreased at around 0.14 mm. The maximum load tested under the wet atmosphere was slightly lower than that under the dry atmosphere.

Figure 3 shows the applied stress as a function of the lifetime to fracture during static fatigue tests at 850°C under dry and wet atmospheres. Lifetimes under both atmospheres increased with a

Fig. 2. Typical Load-displacement curves during three-point bending tests at 850°C under (a) dry and (b) wet atmosphere.

Fig. 3. Stress as a function of the lifetime to fracture during static fatigue tests at 850°C under (a) dry and (b) wet atmosphere. Open circles and dashed lines show the median values of flexural strength distributions under each atmosphere. Closed circles indicate the static fatigue lifetime of each specimen, although those with rightward arrows are data for specimens that survived to the end of the tests. Numerals beside the arrows indicate the number of specimens that survived. Open diamonds indicate the median values of the lifetime distributions.

decrease in stress. The number of specimens that survived tests with an applied stress below 40 MPa under wet atmosphere was fewer than that under dry atmosphere. The static lifetime under wet atmosphere was shorter than that under dry atmosphere, similar to the tendencies observed with respect to flexural strength.

The statistical fatigue limit was estimated using the method reported by Jin et al.^{11)–15)} The flexural strength and residual strength of the specimens that survived the static fatigue tests at 850°C were measured under reducing atmosphere (Ar-4% H₂) to prevent the oxidation of Ni and subcritical crack growth. **Figure 4** shows the median values of residual strength distributions for surviving specimens during static fatigue tests at 850°C as a function of the applied static stress. The dashed lines indicate the median values of the flexural strength distribution tested under a reducing atmosphere (Ar-4% H₂) at 850°C. The intersection of the residual strength and the strength under reducing atmosphere gives the statistical fatigue limit for the specimens under static fatigue loads at 850°C. The fatigue limits under dry and wet atmospheres were 23 and 17 MPa, respectively. The static fatigue limit under wet atmosphere was thus confirmed to be lower than that under dry atmosphere, similar to the tendency observed with respect to flexural strength in the same environ-

Fig. 4. Residual strength of surviving specimens during static fatigue tests at 850°C under (a) dry and (b) wet atmosphere as a function of static stress applied. Open circles and dashed lines indicate the median values of strength under reducing atmosphere.

ments. However, no significant difference between the fracture surfaces of the specimens was evident, and this was independent of the differences in testing conditions, such as the atmosphere and magnitude of the load.

Water vapor accelerates the volatilization of Ni to produce $\text{Ni}(\text{OH})_2$; hence, the reduction of the Ni component in the specimens may induce stress concentration in the porous structure of these specimens. However, the thermodynamic partial pressures of $\text{Ni}(\text{OH})_2$ under dry and wet atmospheres were calculated to be extremely low, at 2.5×10^{-12} and 8.5×10^{-7} Pa, respectively. In addition, although the holding time for the three-point flexure tests was very short (15 min), the flexural strength under wet atmosphere was also lower than that under dry atmosphere. It is thus unlikely that preferential vaporization of the Ni component was responsible for the strength degradation of the specimens.

Although phase transformation of YSZ from tetragonal to monoclinic forms is known to be caused by water vapor percolation, the YSZ component of the Ni-YSZ composite examined in this study was not significantly affected by this because the YSZ phase in the specimens was 100% cubic.⁹⁾ This suggests that the mechanical strength of Ni-YSZ specimens decreases primarily as a result of selective stress corrosion of the YSZ particles. The likely mechanism for this is preferential absorption of H_2O molecules close to the stress concentration zone at the tops of cracks in YSZ grains, similar to mechanisms reported for several oxide ceramics in the literature.^{16),17)}

In summary, the effect of water vapor on the mechanical properties of an Ni-YSZ composite (volume ratio of Ni:YSZ =

40:60) was investigated at 850°C. Both the flexural strength and static fatigue limit of Ni-YSZ obtained from the static fatigue lifetime under a wet atmosphere were lower than those under a dry atmosphere. This can be explained by the absorption of H_2O molecules into YSZ particles leading to accelerated crack growth. In addition, Ni-YSZ was easily fatigued because the fatigue limit values for Ni-YSZ were extremely low, corresponding to almost one-third of that for the flexural strength, regardless of the type of atmosphere.

Acknowledgment This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. NRF-2016M1A2A2940138).

References

- 1) M. Ni, M. K. H. Leung and D. Y. C. Leung, *Int. J. Hydrogen Energy*, **33**, 2337–23 (2008).
- 2) S. Y. Gómez and D. Hotza, *Renew. Sustain. Energy Rev.*, **61**, 155–174 (2016).
- 3) Z. Wang, M. Mori and T. Araki, *Int. J. Hydrogen Energy*, **35**, 4451–4458 (2010).
- 4) R. K. Akikur, R. Saidur, H. W. Ping and K. R. Ullah, *Energy Convers. Manage.*, **79**, 415–430 (2014).
- 5) M. Pihlatie, A. Kaiser and M. Mogensen, *J. Eur. Ceram. Soc.*, **29**, 1657–1664 (2009).
- 6) S. Watnabe, K. Sato, S. Sukinou, F. Iguchi, K. Yashiro, K. Amezawa, H. Yugami, T. Hashida, J. Mizusaki and T. Kawada, *Jpn. Soc. Mech. Eng. A*, **78**, 349–360 (2012).
- 7) H. Kitahara, F. Iguchi, T. Okuda, N. Sata, T. Kawada and H. Yugami, *Jpn. Soc. Mech. Eng. A*, **78**, 1198–1207 (2012).
- 8) S. D. Kim, S. H. Hyun, J. Moon, J. H. Kim and R. H. Song, *J. Power Sources*, **139**, 67–72 (2005).
- 9) K. Matsui, *TOSOH Res. Technol. Rev.*, **55**, 7–18 (2011).
- 10) M. Tanaka, T. Matsudaira, D. Igimi and S. Kitaoka, *J. Mater. Res.*, **26**, 2450–2457 (2011).
- 11) G. Jin, A. Honjoh and H. Awaji, *J. Ceram. Soc. Japan*, **108**, 614–616 (2000).
- 12) H. Awaji, S.-M. Choi and D. Jayaseelan, *J. Ceram. Soc. Japan*, **109**, 591–595 (2001).
- 13) H. Awaji, “Strength of Ceramic Materials” (Serammiku-Zairyokudogaku), Corona Pub. Co. Ltd., pp. 71–86 (2001).
- 14) T. Matsudaira, S. Kitaoka, Y. Kuzushima, H. Awaji and D. Igimi, *J. Soc. Mater. Sci. Jpn.*, **53**, 607–612 (2004).
- 15) T. Matsudaira, Y. Kuzushima, S. Kitaoka, H. Awaji and D. Yokoe, *J. Ceram. Soc. Japan*, **112**, S327–S332 (2004).
- 16) T. Michalske and S. W. Freiman, *J. Am. Ceram. Soc.*, **66**, 284–288 (1983).
- 17) T. Sato and M. Shimada, *J. Am. Ceram. Soc.*, **68**, 356–359 (1985).