A NOVEL METHOD FOR PREPARATION OF Ni/YSZ CERMET
BY VAPOR-PHASE PROCESSES

Takanori OGAWA*, Tsutomu IOROI, Yoshiharu UCHIMOTO
Zempachi OGUMI and Zen-ichiro TAKEHARA
Faculty of Engineering Kyoto University,
Yoshida, Sakyo-ku, Kyoto, 606-01 Japan
*The Kansai Electric Power Co., Inc.,
Nakanoshima, Osaka 530-70 Japan

ABSTRACT
A novel method for preparation of Ni/YSZ cermet was developed. A YSZ
layer was vapor-deposited on NiO or on Ni covered with NiO at 1000 °C
under reduced pressure using ZrCl₄ and YCl₃ as metal sources and NiO as
an oxygen source. The morphology of deposited YSZ was dependent on
the amount of NiO and reaction time. When amount of NiO was small, the
layer was porous and the deposition proceeded only by a chemical vapor
deposition (CVD) process. When the large amount of NiO was used, this
CVD process, which was dominant at the early stage of the reaction, ceased
after closing pores of the depositing YSZ layer and an electrochemical
vapor deposition (EVD) process followed.

INTRODUCTION
Ni/yttria stabilized zirconia (YSZ) cermet is one of the most promising anode
materials for solid oxide fuel cells (SOFCs) and so far has attracted considerable
attention [1,2,3]. This Ni/YSZ cermet has been generally prepared by a slurry method.
Three phase boundary formed by solid oxide electrolyte, gas and electrode is
considered as active sites of the anode [4]. Therefore, it is expected that performance
of SOFC could be improved by increasing the three phase boundary region. Fig. 1 (a)
schematically shows a structure of the cermet anode prepared by a slurry method [5].
Fig. 1 (b) schematically shows the structure of cermet anode which was aimed in this
work. This type of cermet is expected to give a large area of the three phase boundary
and hence to show high performance as an anode for SOFC.

In order to prepare Ni/YSZ cermet of Fig. 1 (b), a new vapor-phase method for
deposition of porous YSZ was devised, e.g., nickel oxide was used as an oxygen
source for the CVD of YSZ using vapors of yttrium chloride and zirconium chloride.

EXPERIMENTAL
Fine porous nickel metal and nickel oxide pellets were used as substrates for
deposition of YSZ. Porous nickel substrates were prepared by sintering commercially
available nickel powder in H2 at 1000°C for 2h, and these substrates were oxidized by heating in air. Nickel oxide pellets were prepared by sintering commercially available nickel oxide powder at 1500°C.

Figure 2 shows a schematic diagram of experimental apparatus. The reactor was made of a quartz glass tube, which was maintained at 1000°C. The tube was equipped with two side arms which were heated independently. A zirconium chloride container was set at 170°C, and a yttrium chloride container at 735°C. The reactor pressure was maintained at 1 Torr. Chloride vapors were supplied to the main part of the reactor using argon as a carrier gas.

Prepared cermet was characterized by X-ray diffraction (XRD) (SHIMADZU XD–D1W), energy dispersive X-ray spectroscopy (EDAX) (HORIBA EMAX–1770), ESCA (SHIMADZU ESCA–850S) and scanning electron microscopy (SEM) (HITACHI S–510).

RESULT AND DISCUSSION

Porous Nickel Substrate

Since nickel oxide has a significant dissociation pressure at 1000°C [6,7], oxygen released from nickel oxide would react with yttrium chloride and zirconium chloride to form YSZ. The formed YSZ deposited on the nickel oxide surface.

The morphology of deposited YSZ layer was observed by SEM. Figure 3 shows the morphology of porous nickel substrate after vapor phase reaction for 30 min. The deposited YSZ layer was porous, and consisted of aggregates of fine particles. From XRD and EDAX data, this layer had a cubic structure and Y2O3/ZrO2 ratio of about 10%. The thickness of deposited YSZ layers was estimated from SEM photographs. The thickness was dependent on reaction time in the range shorter than 15 min. Beyond 15 min, on the other hand, the thickness was almost independent of reaction time.

Nickel chloride was deposited at the cool exit of the quartz glass tube reactor. From these results, the following CVD reaction was inferred for the substrate containing a small amount of nickel oxide.

\[
ZrCl_4 (g) + 2NiO (s) \rightarrow ZrO_2 (s) + 2NiCl_2 (g) \quad [1]
\]

\[
2YCl_3 (g) + 3NiO (s) \rightarrow Y_2O_3 (s) + 3NiCl_2 (g) \quad [2]
\]

Nickel Oxide Pellet Substrates

Fig.4 shows morphology of the nickel oxide pellet after reaction for less than 5 min. A porous YSZ layer deposited on the surface of nickel oxide pellet. It is suggested from the morphology analogous to that of Fig. 3 that the reaction mechanism was same for the two substrates. In the early stage of the reaction, direct reaction of nickel oxide with metal chlorides of Eq. 1 and 2 took place. Porous YSZ layer formed on the substrate or nickel oxide pellet.
When nickel oxide pellets were reacted with the metal chloride vapors for longer time, the morphology of deposited YSZ layer was different. Fig. 5 (a) and (b) show the surface and the cross section of the nickel oxide pellet, respectively, after reaction for 100 min. Contrary to the case of short reaction time, the YSZ layer grew up to large crystallite and the layer was non-porous[8]. As can be seen in Fig. 5 (b), morphology of fractured cross section of the YSZ layer changes from the inner nickel oxide side to the outer metal chloride vapor side. It seems that on the nickel oxide side the YSZ layer consisted of fine particles, while the layer became tight and rigid on the metal chloride side. This indicates that the reaction mechanism has changed during growth of the YSZ layer. An XRD pattern of the layer of Fig. 5 is shown in Fig. 6. This pattern indicates the deposition of cubic zirconia layer. Peaks assigned to metallic nickel appeared after the reaction. Through CVD process of Eq. 1 and 2, no metallic nickel would be formed. This result indicates that following the CVD process of Eq. 1 and 2, an EVD process [8,9,10] took place as described below.

\[
\text{NiO (s)} \rightarrow \text{Ni (s)} + \frac{1}{2}\text{O}_2 (g) \quad [3]
\]

\[
\text{ZrCl}_4 (g) + \text{O}_2 (g) \rightarrow \text{ZrO}_2 (s) + 2\text{Cl}_2 (g) \quad [4]
\]

\[
2\text{YCl}_3 (g) + 3\text{O}_2 (g) \rightarrow \text{Y}_2\text{O}_3 (s) + 3\text{Cl}_2 (g) \quad [5]
\]

CONCLUSIONS

Ni/YSZ cermet was prepared by deposition of porous YSZ layer by reaction of yttrium chloride and zirconium chloride in vapor phase using nickel oxide as an oxygen source. The morphology of deposited YSZ on nickel or nickel oxide as a substrate was found to be dependent on the reaction time and on the amount of starting nickel oxide. The CVD process was dominant in the early stage of the reaction, and the EVD process became predominant after the tight covering of substrate surface with deposited YSZ.

REFERENCES

1. T. Kawada, N. Sakai, H. Yokokawa, M. Dokiya, M. Mori and T. Iwata, J. Electrochem. Soc., 137, 3042 (1990).
2. D. W. Dees, T. D. Claar, T. E. Easier, D. C. Fee and F. C. Morazek, J. Electrochem. Soc., 134, 2141 (1987).
3. P. H. Middleton, M. E. Seiersten and B. H. C. Steele, Proceedings of the First International Symposium on SOFC, p. 90 (1989).
4. E. J. L. Schouler and M. Kleitz, J. Electrochem. Soc., 134, 1045, (1987).
5. T. Kawada, N. Sakai, H. Yokokawa, M. Dokiya, Solid State Ionics, 40/41, 402 (1990).
6. I. Barin, O. Knacke, "Thermochemical Properties of Inorganic Substances", Springer, Berlin (1973).
7. I. Barin, O. Knacke and O. Kubaschewski, "Thermochemical Properties of Inorganic Substances", Supplement, Springer, Berlin (1973).

8. M. F. Carolan and J. N. Michaels, *Solid State Ionics*, 37, 197 (1990).

9. A. O. Isenberg, *Solid State Ionics*, 3/4, 431 (1981).

10. U. B. Pal and S. C. Singhal, *J. Electrochem. Soc.*, 137, 2937 (1990).

Fig. 1 Schematic model of Ni/YSZ cermet by
(a) a slurry method
(b) a vapor-phase method.

Fig. 2 Schematic diagram of an apparatus for preparation of Ni/YSZ cermet by a vapor-phase method.
Fig. 3 Scanning electron micrograph of oxidized porous Ni after vapor-phase reaction with ZrCl$_4$ and YCl$_3$.

Fig. 4 Scanning electron micrograph of NiO pellet after vapor-phase reaction with ZrCl$_4$ and YCl$_3$ for less than 5 min.

Fig. 5 Scanning electron micrographs of NiO pellet after vapor-phase reaction with ZrCl$_4$ and YCl$_3$ for 100 min. (a) surface (b) cross-section

Fig. 6 X-ray diffraction pattern of NiO pellet after vapor-phase reaction with ZrCl$_4$ and YCl$_3$ for 100 min.

- Ni
- NiO
- YSZ