—Communication—
Reaction of SOFC Components with Sealing Materials

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1 INTRODUCTION

One of the technological difficulties of the planar–type Solid Oxide Fuel Cells (SOFCs) is sealing between yttria stabilized zirconia(YSZ) electrolyte and lanthanum chromite separator. Among many ceramics sealing methods[1),2)], melt sealing technique has attracted some interest because gaseous tightness can be expected to achieve easily. For this purpose, one needs such sealing materials that have a low melting temperature or a low glass–transition temperature. Silica–based glass materials have been adopted[3),4)] because of their low glass–transition temperature. However, there remain uncertainties about the chemical compatibilities with SOFC components. In this report, to clarify the chemical nature of the reactions, the reactions and the chemical stability of SOFC components (lanthanum chromite and YSZ) with sealing materials are investigated using a typical borosilicate glass, Pyrex.

2 EXPERIMENTAL

2.1 Materials

Calcium doped lanthanum chromite was prepared by the oxalic salt method[5)]. Metal nitrates, $La(NO_3)_3$, $Ca(NO_3)_2$ and $Cr(NO_3)_3$ were co–precipitated with the following composition: La:Ca:Cr=0.85:0.18:1.0. This solution was dried and then calcined at 1373 K for 5 h in air. Resulting powders were almost single phase, as measured by XRD, which was pressed into pellets (20 mm in diameter, 2 mm thick) at 120 MPa. The pellets were sintered at 1673 K in air to 95 % relative density. Similarly, powders of 8 mol%-Y_2O_3 stabilized ZrO_2 (YSZ, TOSOH–TZ8YS) were pressed into pellets. The Pyrex glass used in this study was a borosilicate glass powder with the composition: SiO_2=81.0 mass %, B_2O_3=13.0 mass %, Na_2O=4.0 mass % and Al_2O_3=2 mass %.

2.2 Reaction Experiment

The surface of sintered pellets (YSZ and calcium doped lanthanum chromite) was polished with diamond paste(3 μm) to obtain flat and smooth planes. A Pyrex green pellet was put between the sintered YSZ and calcium doped lanthanum chromite pellets. This couple was heated at 1273–1473 K for 24–200 h in air under applied pressure of about $5.0×10^{-3}$ MPa. After heating under different experimental conditions, the couples were cut perpendicular to the surface and

then served SEM observation. The reaction products and the composition in the reaction layers were analyzed by EDX with ZAF correction. In addition, reaction products of powder experiments were identified by XRD.

3 RESULTS

3.1 Reaction between YSZ and Pyrex glass

Figure 1 shows a SEM photograph and X–ray maps at the interface between YSZ and Pyrex. The SEM image clearly shows that a new phase was formed at the interface. This phase was mainly $ZrSiO_4$(zircon) as identified by EDX element analysis and XRD. Fig.2 shows element distribution between YSZ and Pyrex glass. Yttrium diffused beyond this reaction layer into the glass phase, whereas relatively a little zirconium was observed in this phase. Thus the main chemical processes can be written as follows;

$$ZrO_2(\text{in YSZ})+SiO_2(\text{in glass})→ZrSiO_4 \quad (1)$$
$$Y_2O_3(\text{in YSZ})=Y_2O_3(\text{in glass}) \quad (2)$$
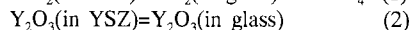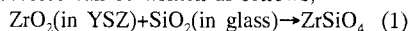
The chemical behavior of sodium and boron was not observed by EDX. Although zircon formation was expected to occur even under 1173 K from the thermochemical estimation, the zircon layer was not observed at this temperature. This is probably due to the low growth rate of the reaction layer at this temperature.

Above 1273 K, the growth of the reaction layer obeyed the parabolic law. The equations obtained were as follows:

$$(x/μm)^2=1.83×10^{-4}(t/s) \quad \text{at 1473 K} \quad (3)$$
$$(x/μm)^2=1.47×10^{-5}(t/s) \quad \text{at 1273 K} \quad (4)$$

The parabolic behavior suggests that some diffusion processes may be the rate–determining step. From these equations, the reaction layers are estimated to grow about 22 μm at 1273 K and 76 μm at 1473 K for 1 year.
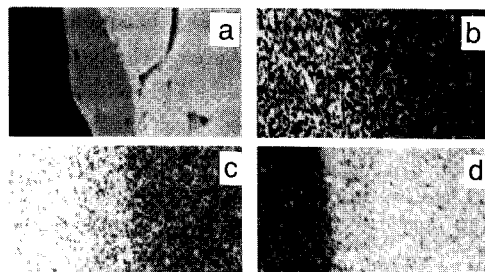

Fig.1 SEM photograph(a) and X–ray maps(b,c,d) of the interface region of YSZ–Pyrex (1473 K, 24 h). left side : Pyrex, right side : YSZ
b: Y(Lα), c: Si(Kα), d: Zr(Lα) |————————|
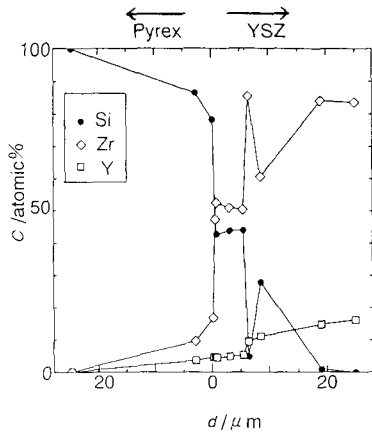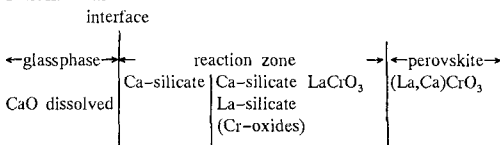   10μm

Fig.2 Element distribution between YSZ and Pyrex.
(1473 K, 48 h, Na, B were omitted).

3.2 Reaction between calcium doped lanthanum chromite and Pyrex glass

Figure 3 shows a SEM photograph and X-ray maps at the interface between calcium doped lanthanum chromite and Pyrex. The joining was accomplished by the formation of a thick new phases at the interface. Fig.4 shows element distribution at the interface between lanthanum chromite and Pyrex. Due to many elements involved, the diffusion profile was more complicated than that of YSZ–Pyrex. From Fig.3 and Fig.4, we can define three zones at the interface vicinity: (1)the glass phase in which some components in the perovskite phase dissolved, (2)reaction zone, and (3)the perovskite phase from which some components migrated. The most striking features is the migration of the calcium component. The chemical nature associated with this migration can be summarized as follows: (1)In the perovskite layer, some Ca–depleted areas were observed. This depletion was supposed to be caused by the migration of $CaCrO_3$ in the perovskite. (2)In the reaction zone, calcium tends to diffuse further to form calcium silicate at the boundary between the glass phase and the reaction zone. The thin Ca condensed layer had the composition: Ca:Si=0.4:0.6. (3)In the glass phase, calcium dissolved to some extent. In this process, chromium component does not migrate together with the calcium component, whereas it remains in the reaction zone. Silicon does not dissolve into the perovskite phase. This means that the silicon component migrates in the reaction zone by reacting with the La–, Ca–components to form some silicates. From the above consideration, the following reaction scheme can be derived:

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                    interface
←–glassphase→|←–      reaction zone      →|←–perovskite→
             |Ca–silicate|Ca–silicate LaCrO₃|(La,Ca)CrO₃
CaO dissolved|           |La–silicate       |
             |           |(Cr–oxides)       |
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The important point to be solved is that the behavior of the chromium component is not clarified. Some parts of the chromium should remain as the chemical form of $LaCrO_3$. However, Ca and La in the

perovskite reacted with silica to form silicates. This means that the corresponding amount of the Cr component should come out of the perovskite phase. The present EDX analysis shows that this chromium remained in the reaction zone. The chemical form of the chromium may be Cr_2O_3 or Na_2CrO_4. Note also that, in the XRD pattern for powder experiments, it was hard to identify the chemical forms of the lanthanum compounds.
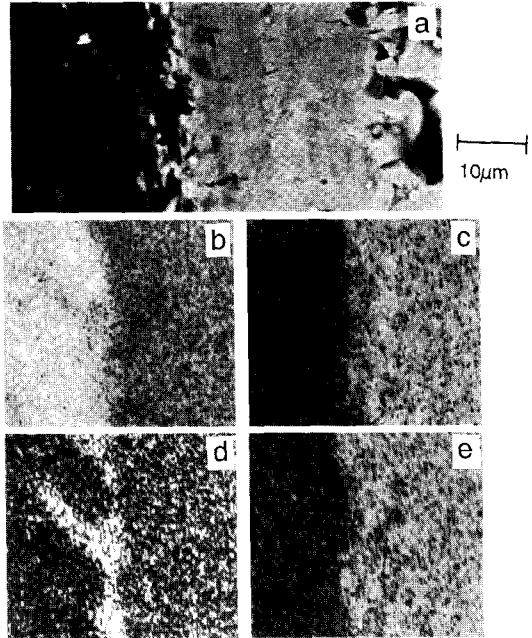

Fig.3 SEM photograph(a) and X–ray maps
(b–e: 1473 K, 48 h) of the interface region of lanthanum chromite and Pyrex.
left side : Pyrex
right side: Lanthanum Chromite
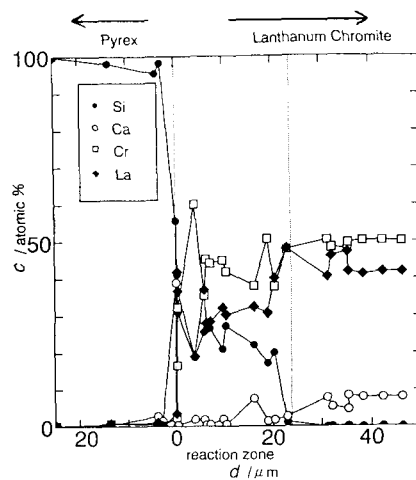b: Si(Kα), c: Cr(Kα), d: Ca(Kα), e: La(Lα)

Fig.4 Element distribution between lanthanum chromite and Pyrex.(1473 K, 48 h)

Similar to the reaction of YSZ–Pyrex, the reaction layer grew with reaction time. However, the growth rate didn't follow the parabolic law as shown in Fig.5. The growth of the reaction layers was rather quick and more complicated than that of YSZ–Pyrex. The reaction layer grew about 7.5 μm at 1273 K for 200 h.

In powder reaction of lanthanum chromite with Pyrex, many phases were found. The identified phases were $CaSiO_3$, Ca_2SiO_4, $CaCrO_4$, $CaCr_2O_4$ and there remained undefined phases. According to the earlier reports[6)-8)], the above phases were found in the system CaO–chromium oxide–SiO_2. However the identified phases in the powder experiments were somewhat different from those of the pellet experiments. The calcium content observed by EDX in the reaction layer was lower than expected by the powder reaction. Further research will be needed to know these reactions.
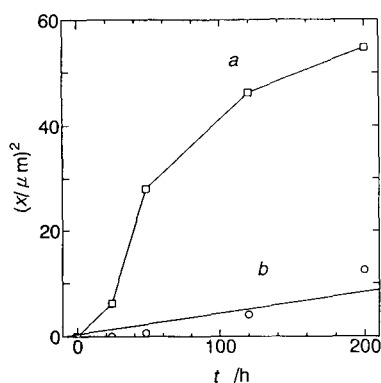

Fig.5 Growth rate of the reaction layers.(1273 K)
    a: Lanthanum Chromite–Pyrex
    b: YSZ–Pyrex

4 DISCUSSION

In this study, the SOFC components joined with Pyrex glass with no voids and cracks. Note however, that the sealing was made by the formation of silicates. This is not appropriate for "melt" sealing, because this technique is based on an idea that sealing materials should be "reproducible melt" under the SOFC operation. In addition, the thermal expansion mismatch between the reaction layer and SOFC components should be taken into consideration. For example, zircon has lower thermal expansion coefficient[9)](4.1×10^{-6} K^{-1}) than that of zirconia ($\approx 10 \times 10^{-6}$ K^{-1}).

To avoid forming the reaction layers, possible ways are:(1)lowering the silicon activity by changing the composition of glass, or (2)coating the SOFC component surfaces by inactive substances. In case of zirconia, the zircon formation can be reduced by controlling the silicon activities. In case of lanthanum chromite, against which the chemical reaction is severer, on the other hand, the possible way may be the coating by an inactive substance.

Another problem of using silica–based glass is that diffusion of the basic oxides (Y_2O_3 and CaO) from the SOFC components to Pyrex glass occurs significantly. This change of the glass composition will lead to some degradation of sealing property.

5 CONCLUSION

YSZ easily reacted with Pyrex to form $ZrSiO_4$. The growth of $ZrSiO_4$ layers followed the parabolic law. Lanthanum chromite also easily reacted with Pyrex, to form calcium silicate and calcium chromium oxide phases. The thermal expansion mismatch between them will affect the long–term stability of sealed parts.

Basic oxides such as CaO and Y_2O_3 easily diffused from original SOFC components to Pyrex glass because of their affinities of silicon. The diffusion of these compounds leads to the alteration of Pyrex with changing its composition.

The melt sealing technique contains many problems as reported above. For solving the problems, the following ways are needed:(1)coating the SOFC components by an inactive substance, (2)making a new glass materials inactive to the SOFC components.

REFERENCES

1)S.V.Phillips, A.K.Datta and L.Lakin, Proceedings of the Second International Symposium on SOFCs (Athens, Greece, July 1991), pp.737–745, Edited by G.Grotz, P.Zeger, S.C.Singhal and O.Yamamoto, Commission of the European Communities, Luxembourg, 1991.
2)M.L.Santella, CERAMIC BULLETIN, 71[6], 947–954, (1992).
3)W.Dönitz, E.Erdle, W.Schäfer, R.Shcamm and R.Späh, Proceedings of the Second International Symposium on SOFCs (Athens, Greece, July 1991), pp.301–304, Edited by G.Grotz, P.Zeger, S.C. Singhal and O.Yamamoto, Commission of the European Communities, Luxembourg, 1991.
4)S.Murakami, Y.Akiyama, N.Ishida, T.Yasuo, S.Taguchi, T.Sato and N.Furukawa, Proceedings of International Fuel Cell Conference (Makuhari, Japan, February 1992), pp.301–304, hosted by NEDO, Japan, 1992.
5)N.Sakai, T.Kawada, H.Yokokawa, M.Dokiya and I.Kojima, J. Am. Ceram. Soc., 76[3], 609–616 (1993).
6)N.Sakai, T.Kawada, H.Yokokawa and M.Dokiya, Proceedings of International Fuel Cell Conference (Makuhari, Japan, February 1992), pp.365–368, hosted by NEDO, Japan, 1992.
7)D.Smith, M.Sayer, P.Roeder, A.Smith and P.Odier, J. Am. Ceram. Soc., 72[2], 308–311 (1989).
8)J.P.R. de Villiers and A.Muan, J. Am. Ceram. Soc., 75[6], 1333–1341 (1992).
9)F.A.Hummel, J. Am. Ceram.Soc., 33[3] 102–107 (1950).