Joining of Lanthanum Chromite and Yttria Stabilized Zirconia in Sealing of Planar Solid Oxide Fuel Cell

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Abstract The planar solid oxide fuel cell(SOFC) contains several ceramic materials depending on its structure and has refractory metal parts for manifolds, shrouds and current leads. Among ceramic materials for planar SOFC, joining of lanthanum chromite separator and yttria stabilized zirconia(YSZ) electolyte in planar SOFC stack to give strong gas tight seals is necessary for satisfactory operation and high performance. Nevertheless, for planar SOFCs, how to seal the cell stack and gas manifold remains as one of the unsolved problems. Therefore, in this study, we investigated the joining of sintered lanthanum chromite and YSZ pellets using unsintered lanthanum chromite green films as sealent. Scanning electron microscopy(SEM) and energy dispersive X-ray analysis(EDX) revealed that Ca in the sealing material diffused and dissolved into YSZ and sintered lanthanum chromite, and unsintered lanthanum chromite green films reacted with YSZ to form a new phase at the interface. Also, the densification of unsintered lanthanum chromite green films was impeded by the Ca migration.

1. Introduction

The planar SOFCs have features such as high performance, high power density, high efficiency, low emission, and reduced manufacturing cost. Among these factors, the high power density and the low manufacturing cost are the decisive advantages over tubular SOFCs. We have focussed our attention upon these advantages and started the research and development of planar SOFCs, recently. The solid-state electrochemical cell, so-called SOFC, is assembled by using a thin impermeable oxide ion conducting electrolyte which separates porous air electrode(cathode) and porous fuel electrode(anode) compartments. And, for connecting unit cells in series and for separating the air and fuel compartments, a separator, or an interconnector, is placed between unit cellsa.

This SOFC is operated at temperatures as high as 1000℃, and the compatibility and sealing of the constituent materials are very important as one of factors governing the lifetime. Therefore, improvements in conventional gas seal technology are required to develop advanced planar SOFCs. One of the technological difficulties of planar SOFCs is sealing between lanthanum chromite separator and YSZ electrolyte. The joining methods applicable to large scale ceramic sealing are the techniques of diffusion, brazing, cofiring(green bonding) and glass or glass-ceramic joining[1,2].

Among the above mentioned joining methods, we chose the first one because joining method based on diffusion process is suitable for gaseous tightness. This method is a kind of melt sealing method by melt of unsintered lanthanum chromite, and melt sealing technique has attracted some interest because gaseous tightness can be expected to be achieved easily. For this purpose, one needs such methods and sealing materials that have a low melting temperature.

Therefore, joining a cell stack into one monolithic body is considered to be one of the solu-

tions for planar SOFC since the one-step cofiring processes do not show any promising result, joining after separately sintered, in other words, the multi-step cofiring is becoming an attractive process[3]. However, according to our experience this process contains several problems because of the difficulty in joining already sintered ceramics. We found some

kind of lanthanum chromites can be used as joining aid. The aim of this experiment is to clarify the reliability of this process.

2. Experimental

2.1 Materials and Sample Preparation

The compositions and preparation conditions of the samples are summarized in Table 1. The

Table 1. Sample compositions and preparation conditions.

Sample No.	Composition(mol%)	Preparation Method	Sintering Condition
YSZ	$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$	Spray-dry	1400℃, 5h, in air
LCC1	$La_{0.8}Ca_{0.23}CrO_3$	Oxalic salt	1600℃, 5h, in air
LCC2	$La_{0.8}Ca_{0.22}CrO_3$	Oxalic salt	1600℃, 5h, in air
LC33	$La_{0.7}Ca_{0.33}CrO_3$	Doctor blade	green film(t=1500μm)
LC36	$La_{0.7}Ca_{0.36}CrO_3$	Doctor blade	green film(t=400μm)

YSZ powders used for the electrolyte material were 8 mol% Y_2O_3 stabilized ZrO_2(TZ8YS : BET surface area about 5 m²/g, manufactured by Tosoh Corporation). In the spray-dry method adopted by Tosoh, appropriate amounts of ZrO_2 and Y_2O_3 powders were mixed and calcined at 1000℃. The YSZ powders were uniaxially cold pressed into pellets at 30 MPa using a starch binder.

Calcium-doped lanthanum chromite used as a separator was prepared by the oxalic salt method[4]. Metal nitrates, $La(NO_3)_3$, $Ca(NO_3)_2$ and $Cr(NO_3)_3$ were co-precipitated with the following compositions, respectively; La : Ca : Cr=0.8 : 0.23 : 1.0(LCC1), 　 0.8 : 0.22 : 1.0 (LCC2). We chose the two compositions because 2~3 mol% Ca excess in LCC is enough to facilitate densification of the LCC at a low temperature in air[5,6] and the value of thermal expansion coefficient of LCC is in a good agreement with that of YSZ[7,8,9]. This solution was dried and then calcined at 1000℃ for 10 h in air. Resulting powders were also pressed into pellets. The relative density(d/d_0) of YSZ and LCC was more than 95% and 94%, respectively, where d is a measured sample density and d_0 is the theoretical density determined from the lattice parameter and the

chemical formular of each sample.

For sealing materials, the green films of LC33 and LC36 were prepared by a doctor blade method[10,11]. The composition of slurry was somewhat adjusted depending on the powder, the base composition being 10 g of polyvinyl butyral, 10 cm³ of dibutyl phthalate, 2 cm³ of fish oil, 2 cm³ of polyethylene glycol mono-p-iso-octyl phenyl ether(Triton X-100), 30 cm³ of isopropanol, and 15 cm³ of toluene per each powder of 10 g. Also, the thickess of LC33 and LC36 green film was 1500 μm and 400μm, respectively. The excess Ca was added in the separator and sealing material to enhance sinterability[5,6].

2.2 Diffusion Couple Experiment

The stacking and coupling conditions of diffusion coupling samples are summarized in Table 2. The surfaces of sintered pellets(YSZ and LCC) were polished with diamond paste(1 μm) to obtain flat and smooth planes. The LC (LC33 and LC36) green films were put between the sintered YSZ and LCC(LCC1 and LCC2) pellets, respectively. One group of diffusion couples[(sample 1) and (sample 2)] were heated at 1200℃ for 10h in air under applied pressure of about 2.0×10^{-2} MPa and 3.0×10^{-2} MPa, respectively. The other diffusion

Table 2. Stacking and coupling conditions of diffusion coupling samples.

Sample No.	Stacking	Coupling condition
Sample 1	LCC1/LC33/YSZ	1200℃, 10h, 2.0 × 10⁻² MPa, in air
Sample 2	LCC1/LC36/YSZ	1200℃, 10h, 3.0 × 10⁻² MPa, in air
Sample 3	LCC2/LC33/YSZ	1400℃, 2h, 3.0 × 10⁻² MPa, in air
Sample 4	LCC2/LC36/YSZ	

couples[(sample 3) and (sample 4)] were heated at 1400℃ for 2h in air under applied pressure of about 3.0×10^{-2} MPa.

After heating under different experimental conditions, the couples were cut perpendicular to the surface and then subjected to SEM(S-800, Hitachi Co. Ltd., Japan) observation. The reaction products and the composition in the reaction layers were analyzed automatically with an EDX(Kevex Co. Ltd., U.S.A.) using the standardless Gaussian deconvolution and ZAF correction. In addition, the reaction products in the difffusion couples were identified by a XRD(PW-1800, Phillips Co. Ltd., Netherlands).

3. Results and Discussion

3.1 Reaction between YSZ and LC(LC33 and LC36)

The sealing material used in the SOFC is calcium-doped lanthanum chromites. Lanthanum chromite is known to be difficult to densify under conditions suitable for the other components of the SOFC[12]. A common approach to improving densification of lanthanum chromite is to use liquid phase sintering. During liquid phase sintering, a liquid phase coexists with the solid powder during some part of the thermal cycle. The liquid phase enhances the mass transport during sintering, resulting in improved densification. The liquid phase may be transient or persistent during sintering, depending on the solubility relationship.

Dopants can form a transient liquid phase during firing and enhance the densification by liquid phase sintering[13, 14, 15]. The densification of unsintered calcium-doped lanthanum chro-

mite green films as sealent can be contributed to the presence of Ca-Cr-O melts[16]. According to the phase diagram of Penek[17], a Ca-Cr-O-base oxide has a liquid phase above 1022℃ for the composition with a Ca/Cr ratio of about 1. The function of liquid phase as a sintering aid is to pull the particles closer together by surface tension forces and to enhance diffusion of the solid phase to points of particle-to-particle contact to promote densification.

Therefore, introduction of a liquid phase sintering aid encourages densification of unsintered calcium-doped lanthanum chromite green films and joint of YSZ and LCC.

Photo. 1 shows the SEM photograph and X-ray maps at the interface between YSZ and LC33 of sample 1. The SEM image clearly shows that a new phase was formed at the interface between YSZ and LC33. The new phase mainly consisting of Zr, Y and Ca metals was formed in the YSZ side, not in the LC33 side. This means that La, Ca and Cr, the components of the LC33, diffuse into the YSZ and produce the $CaZrO_3$ phase containing little amounts of other elements. Fig. 1 shows various elemental distibutions around the interface region between YSZ and LC33 of sample 1. Due to the number of elements involved, the diffusion profile was more complicated than that of the LCC/LC33 in the following section.

From Photo. 1 and Fig. 1, we can define three zones at the interface vicinity : (1) the YSZ phase into which some components from the perovskite phase dissolved, (2) the reaction zone, and (3) the perovskite phase from which some components migrated out. The most important observation is the migration of Ca component. The chemical nature associated
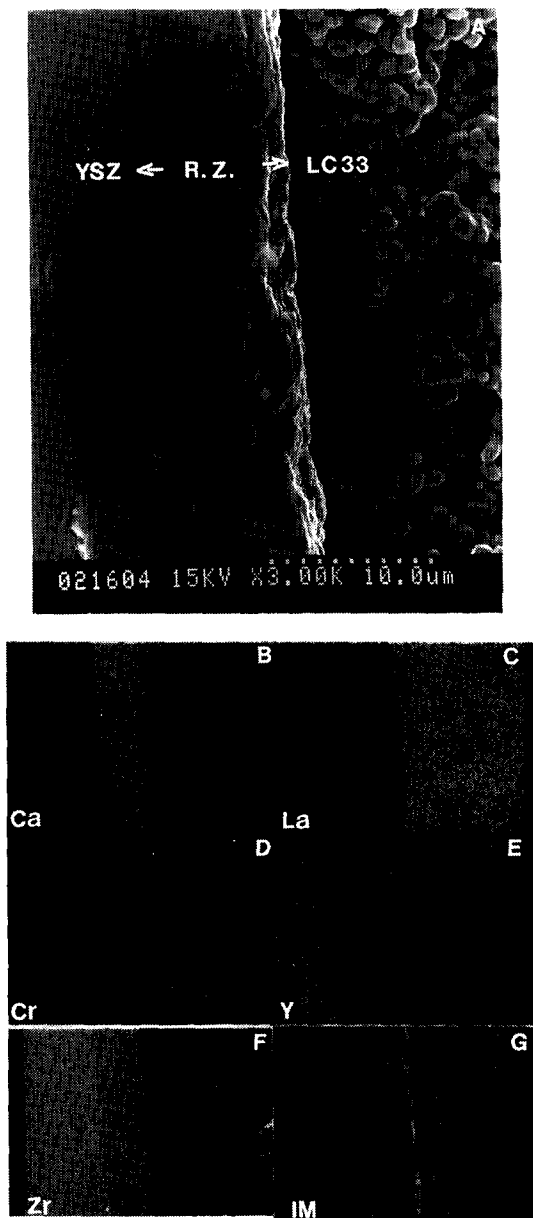
Photo. 1. SEM photograph(A), X-ray maps(B-F) and SEM image(G) of the interface region of LC33/YSZ of sample 1(1200℃, 10h, 2.0×10⁻² MPa).

with this migration can be summarized as follows. First, in the perovskite layer, some Ca-depleted areas were observed. This depletion was supposed to be caused by the migration of CaCrO₃ in perovskite. When the calcium-doped lanthanum chromite green films are sintered

singly, Ca and Cr in the liquid phase are taken into the bulk of calcium-doped lanthanum chromite particle as the temperature increases, and ultimately excess Ca is left as CaO. When the calcium-doped lanthanum chromite green films are brought into contact with the sintered body of YSZ, the function of the liquid phase as a sintering aid can not be expected because the liquid phase moves to the YSZ side. Only Ca dissolves into the YSZ phase from the Ca-Cr-O oxide in the calcium-doped lanthanum chromite porous body. Therefore, Cr oxide or Cr rich Ca-Cr-O phase is left. Secondly, in the reaction zone, Ca is concentrated in the newly formed phase. In order to identify the compound, XRD analysis was carried out for the pellet surface and the YSZ surface after removing the oxide sealing material. The results are shown in Fig. 2. The compound formed in the interface was found to be $CaZrO_3$. From the results in Photo. 1, Fig. 1, and 2, it is shown that the only compound formed at 1200 ℃ is $CaZrO_3$ containing small traces of La, Cr
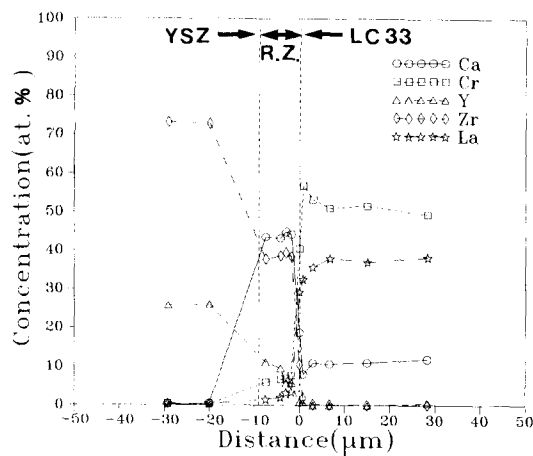

Fig. 1. Elemental distribution between YSZ and LC33 of sample 1 (1200℃, 10h, 2.0×10⁻² MPa)

and Y. Thus, the order of the phases became as follows : LC33/CaZrO₃(La, Cr, Y)/YSZ. Also, Ca tends to diffuse further to form $CaZrO_3$ at the boundary between the YSZ phase and the reaction zone. Thirdly, even in
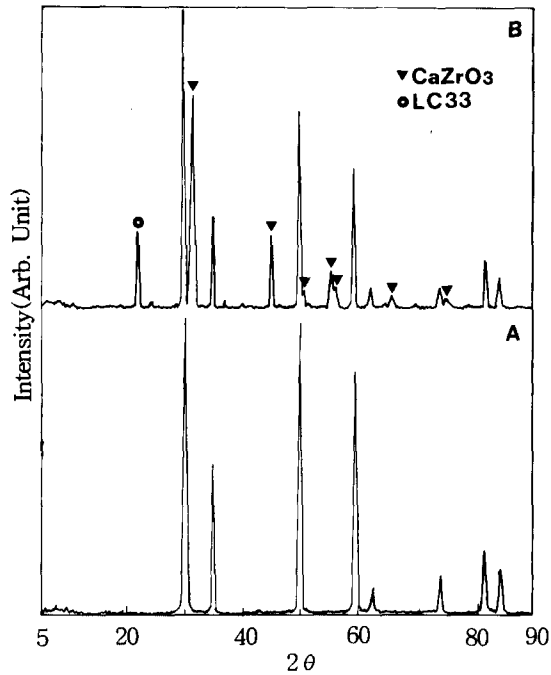
Fig. 2. XRD patterns of YSZ(A), the YSZ surface of which the LC33 was taken off from the LC33/YSZ asembly fired at 1200℃ for 10h(B).

the YSZ phase, Ca dissolved to some extent.

The analysis suggests that the diffusion rate of Ca in the YSZ phase is far slower than in the $CaZrO_3$ phase. In the process, Cr and La components do not migrate along with the Ca component throughout the reaction zone. Zr is not found in the perovskite phase. This means that most of the Zr component migrated into the reaction zone is reacting with Ca component to form $CaZrO_3$. From the above consideration, the following reaction scheme can be derived:

The important point to note is that the behavior of the Cr and La component is not clarified. Some parts of Cr and La should remain as in the form of $LaCrO_3$ or $LaCa_1 {}_xCrO_3$. Since Ca reacted with ZrO_2 to form $CaZrO_3$, the corresponding amount of the Cr and La components should come out of the perovskite phase. The present EDX analysis shows that this Cr and La remained in the reaction zone. The chemical forms of the Cr and La may be Cr_2O_3, $Ca_{1-x}Cr_2O_4$ or La_2O_3.

Similarly, the reaction between YSZ and LC36 of sample 2 was also investigated. The resulting phenomena were similar to that of

	Interface		
YSZ phase	Reaction zone		Perovskite phase
$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ CaO dissolved	Ca_xZrO_3	Ca_xZrO_3 $LaCa_{1-x}CrO_3$(or $LaCrO_3$) $Ca_{1-x}Cr_2O_4$(or Cr_2O_3) La_2O_3	(La, Ca) CrO_3

the reaction between YSZ and LC33 of sample 1. The only difference was the thickness of the reaction zone. The thicknesses of LC33/YSZ of sample 1 and LC36/YSZ of sample 2 were about 9.5 μm and 7.5 μm, respectively. But the cases of diffusion couples of sample 1 and 2 were not found to have proper joints due to poor sinterability of LC caused by the low sintering temperature and Ca migration. So, we investigated the joining of diffusion couples under the applied pressure of 3.0×10^{-2} MPa in the same sintering conditions. The applied pressure dose not affect joining. Also, we in-

vestigated the diffusion coupling sample of 3 and 4 at a higher sintering temperature.

Photo. 2 shows the SEM photograph and X-ray maps at the interface between YSZ and LC33 of sample 3. It is seen that a melt phase in the LC33 is observed as a dark area and this melt phase is observed as a dark glassy compound which mainly contained Ca and Cr. The SEM image also shows that the thickness of new phase increased to about 33 μm and the surface was not clean. Thus, the elemental distribution of this couple was examined to see the reason. The result is shown in Fig. 3,
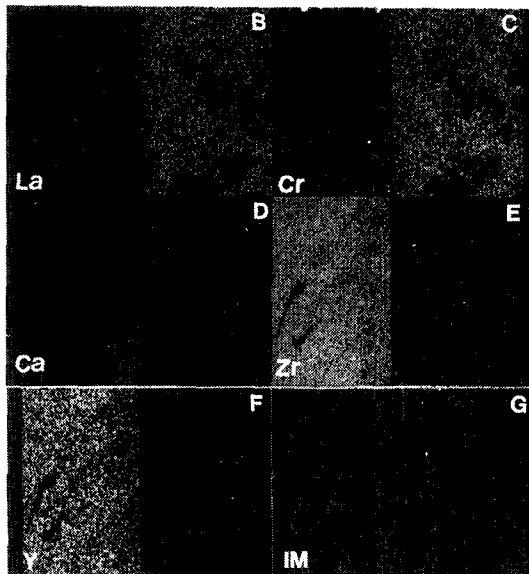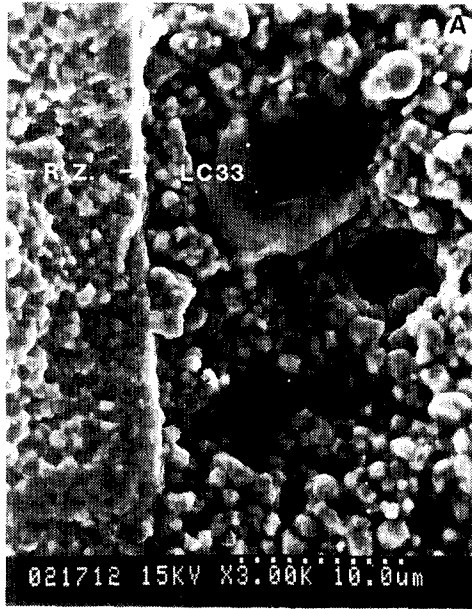
Fig. 3. Elemental distribution between YSZ and LC33 of sample 3 (1400°C, 2h, 3.0×10^{-2} MPa)

Photo. 2. SEM photograph(A), X-ray maps(B-F) and SEM image(G) of the interface region of LC33/YSZ of sample 3(1400°C, 2h, 3.0×10^{-2} MPa).

where the amounts of Cr component is found to be increased in the newly formed phase.

Similarly, the reaction between YSZ and LC36 of sample 4 was also investigated. The results were similar to reaction between YSZ and LC33 of sample 1, except a slight decrease
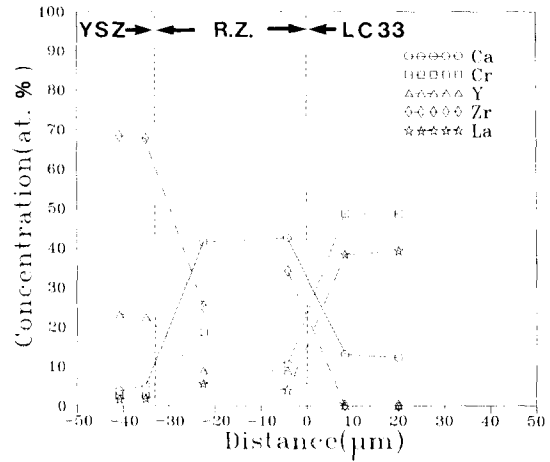
in the thickness of the reaction zone down to about 3.5 μm.

Thus, to clarify the thickness difference of the reaction zone, diffusion coupling samples were also investigated from the standpoint of diffusion[18,19]. For the LC/YSZ couple, the new phase, $CaZrO_3$, was formed at the interface at least at 1200°C. This couple, which is just like a diffusion couple, can be used for determining the rate constant of the formation of the new compound. When the rate constant in a liquid-solid state reaction is governed by diffusion, the thickness of the newly formed phase, X, obeys the parabolic rate equation, $X^2 = 2K_p t$, where K_p is the rate constant and t is time. For the LC33/YSZ and LC36/YSZ couple, the thicknesses of the $CaZrO_3$ for the samples heated at 1200°C were 9.5 μm and 7.5 μm, respectively, while they were 33 μm and 3.5 μm, respectively for the samples heated at 1400 °C. The curves for $\log K_p$ vs. 1/T enable calculation of the activation energy for diffusion of the rate determining mobile ion. The values of the activation energy for LC33/YSZ and LC36 /YSZ are calculated to be about 426.0 kJ/mol and 9.6 kJ/mol, respectively. From these data, it is known that the thickness increase of the

$CaZrO_3$ layer in the LC33/YSZ case is due to the effect of sintering temperature rather than that of sintering time, while the thickness decrease for LC36/YSZ is due to sintering time rather than sintering temperature. But, among the diffusion coupling sample 3 and 4, only LC33/YSZ of sample 3 was found to have proper joining occured. From this, it is known that joining was accomplished by the formation of thick new phases at the Interface.

3.2 Reaction between LCC and LC(LC33 and LC36)

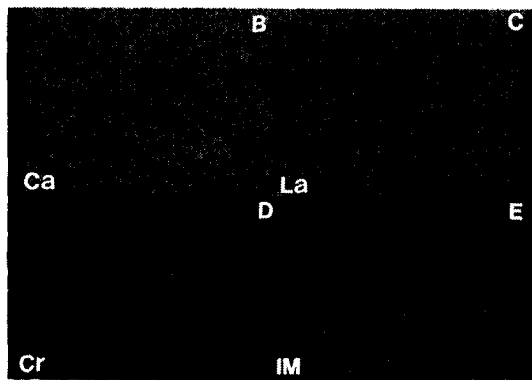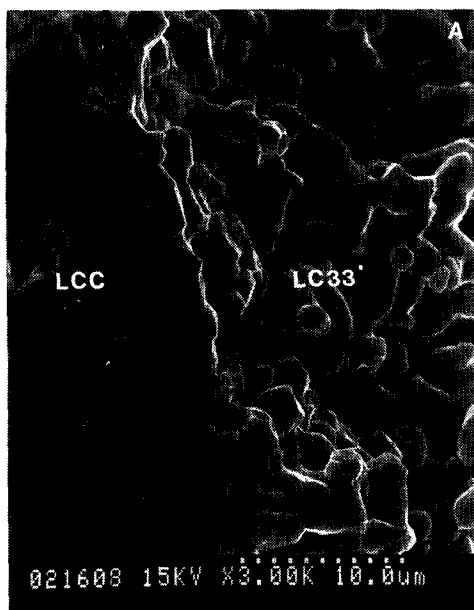The sintering pellets of LCC were almost

Photo. 3. SEM photograph(A), X-ray maps(B-D) and SEM image(E) of the interface region of LCC /LC33 of sample 1(1200℃, 10h, 2.0×10⁻²MPa)

comprised with a single phase of $La_{1-x}Ca_xCrO_3$, as measured by XRD. The X-ray diffractometric results have revealed that in addition to the normal perovskites($La_{1-x}Ca_xCrO_3$), Ca-excess perovskites can exist as a single phase in the composition $x = 0.23$ and 0.22, although the excess of Ca is small. In Photo. 3, these Ca-excess perovskites show also a good sinterability even in air at 1200℃.

Photo. 3. shows the SEM photograph and X-ray maps at the interface between LCC and LC33 of smaple 1. In this couple there is a distinct interface. But, reaction zone does not exist. Sakai et al., who attempted a liquid-phase-assisted sintering of calcium-doped lanthanum chromites, have recently reported that a second phase exists in the form of $CaCrO_4$ or La_2CrO_6 before sintering of $La_{1-x}Ca_xCrO_3$. At around 1100℃, the second phase changes to $Ca_m(CrO_4)_n$, and subsequently reacts with $La_{1-x}Ca_xCrO_3$ grains and enhances their grain growth and particle joining[4]. From this report and Photo. 3, it is seen that LC33 particles were sintered with the surrounding second particles and bonded well to the LCC pellet, and a chemical reaction was occured at the LCC/LC33 interface. Also, in comparison, it is seen that LC33 side of the coupled LCC/LC33 shows enhanced grain growth and sinterability rather than that of the coupled LC33/YSZ of Photo. 1. The reason is due to the same perovskite structure that both LCC and LC have.

Fig. 4 shows elemental distribution between LCC1 and LC33. From Ca profile, it is seen that Ca concetration of LC33 is decreased because of the migration of Ca into LCC1. In Fig. 4, point A is regarded as a grain boundary region of $La_{1-x}Ca_xCrO_3$. Thus, the increase of Ca concentration of point A is due to the Ca-rich substance remained in the vicinity of the grain boundary of $La_{1-x}Ca_xCrO_3$. It was supported by Sakai et al.[4] who observed that AES(Auger Electron Spectroscopy) depth profile on the fractured surface of $La_{0.7}Ca_{0.3}Cr_{1-y}$
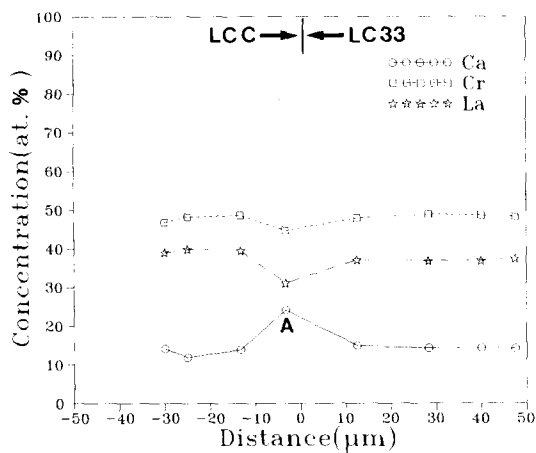
Fig. 4. Elemental distribution between LCC1 and LC33 of sample 1 (1200℃, 10h, 2.0×10^{-2}MPa)

O_3 pellet sintered at 1300℃ shows that the calcium content is higher in the vicinity of the grain boundary. The results were similar to those of reactions between LCC and LC of
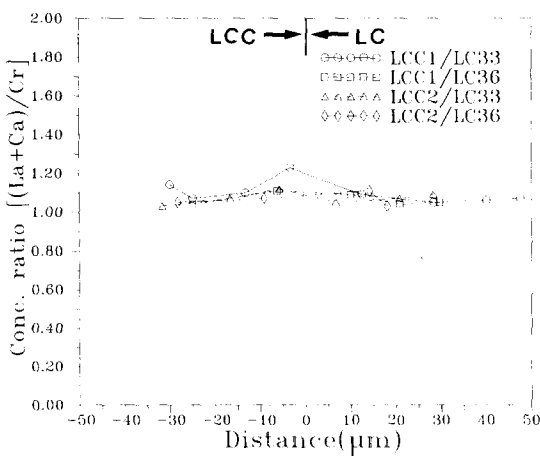

Fig. 5. Elemental ratio of (La+Ca)/Cr between LCC and LC

sample 2, 3 and 4. Fig. 5 shows elemental ratio of (La+Ca)/Cr between LCC and LC. It is seen that the (La+Ca)/Cr ratio was slightly greater than unity in the region near the interface and almost flat elsewhere. It was also clearly shown that the elemental distribution is due to the migration of Ca into LCC.

This diffusion joining method strictly does not depend on the formation of a liquid phase at any stage, being a solid state process. But, in this case of LC as a sealant at 1200℃ and 1400℃, the densification of LC was assisted by $Ca_m(CrO_4)_n$ liquid phase and joined with YSZ and LCC. Note, however, that the sealing was made by the formation of thick $CaZrO_3$ and the densification of LC green films was impended by Ca migration into YSZ and LCC. This is not appropriate for "melt" saling, because this technique is based on an idea that sealing materials should be "reproducible melt" under the SOFC operation. Also, if the joining aids such as LC are introduced, for a satisfatory diffusion joining it requires a similarity of expansion characteristices of the two components. Recently, Mori et al. Have reported that thermal expansion coefficient increases with increasing Ca content in $La_{1-x}Ca_xCrO_3$ and that of $La_{0.7}Ca_{0.3}CrO_3$ is 11.9×10^{-6}/℃[7]. From this report, in our exrerimental case, LC has higher thermal expansion coefficient than that of YSZ(10.5×10^{-6}/℃)[8,9]. Thus, when a low-temperature sinterable unsintered lanthanum chromite containing excess calcium is used for sealing, a consideration must be given to restricting the movement of the melted body and matching the thermal expansion cofficient of the components. To avoid formation reaction layers and to match thermal expansion coefficient, possible ways to be taken are : (1) lowering the Ca activity by changing th composition of unsintered lanthanum chromite, or (2) coating the SOFC component surfaces by inactive substances.

4. Conclusion

In this study, the joining of the stack was attempted by multi-step cofiring using unsintered lanthanum chromite green films as sealent. YSZ easily reacted with a unsintered lanthanum chromite to form $CaZrO_3$, and the joining was accomplished by the formation of thick $CaZrO_3$ layers at the interface. As sintered lanthanum chromite also easily reacted with a unsintered lanthanum chromite due to

Ca migration. And, it is seen that the LC side of the coupled LCC/LC enhanced the grain growth and sinterability rather than that of the coupled LC/YSZ. However, in the melt sealing technique, it revealed that there are problems of the deterioration of YSZ and difficulties in sintering LC due to the diffusion of Ca from LC to YSZ and LCC. To solve the problems, the following measures might be considered : (1) coating the SOFC components by an inactive substance, (2) making a new unsintered lanthanum chromite inactive to the SOFC components.

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