

Reactions at the Calcium Doped Lanthanum Chromite–Yttria Stabilized Zirconia Interface

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Solid oxide fuel cell materials calcium doped lanthanum chromite (La,Ca)CrO₃ and yttria stabilized zirconia (YSZ) are known to interact with each other. This interaction causes interruption of cosintering processes and the formation of secondary phases which degrade fuel cell performance. The present study shows by X-ray diffraction and microscopic analysis that Ca migrates via an exsolved Ca–Cr–O liquid phase emanating from (La,Ca)CrO₃ and reacts with YSZ to obtain an intermediate layer of CaZrO₃. The width of the CaZrO₃ reaction region was found to increase with increasing Ca content in the exsolved Ca–Cr–O second phase. Calcium zirconate was observed to react with YSZ along the YSZ grain boundaries, eventually digesting YSZ grains into a CaZrO₃ matrix. The results demonstrate the improbability of cosintering (La,Ca)CrO₃ and YSZ in the presence of the Ca–Cr–O liquid phase and illustrate the importance of obtaining single phase (La,Ca)CrO₃ to achieve compatibility with YSZ. © 1996 Academic Press, Inc.

1. INTRODUCTION

The interconnect in the solid oxide fuel cell (SOFC) has a twofold purpose of separating air and fuel gases and electrically connecting cells together. High temperature SOFCs operate at a nominal temperature of 1000°C. At this temperature, the interconnect must maintain chemical and mechanical stability, high electronic conductivity ($\sigma_e > 1$ S/cm), and low ionic conductivity ($\sigma_i \leq 0.01$ S/cm) in oxygen partial pressures ranging from 1 to 10⁻²⁰ atm. The interconnect must also have thermal expansion characteristics similar to the other cell components during heating and cooling cycles. Perovskite (La,Ca)CrO₃ has been studied as a prospective interconnect material since it possesses the above material properties.

Historically chromites have been difficult to sinter, but it was recently found that (La,Ca)CrO₃ can be sintered in air at

temperatures as low as 1300°C through the aid of a transient liquid phase belonging to the CaO–Cr₂O₃ phase system (1). At temperatures below 1000°C and when the total Ca content exceeds 25 at%, CaCrO₄ exsolves from (La,Ca)CrO₃ as a secondary phase (2). This secondary phase melts incongruently at 1022°C, forming a liquid and solid mixture (3). By incorporating excess A-site cations (referring to the ABO₃ notation) into the composition of (La,Ca)CrO₃, the sintering characteristics of the liquid phase are enhanced to produce sintering densities greater than 95% of the theoretical value. After densification is complete, the secondary liquid phase should dissolve into (La,Ca)CrO₃.

Unfortunately, when using the above sintering method, this liquid phase migrates from (La,Ca)CrO₃ and reacts with other SOFC components. Cosintering examinations (4, 5) reported that Ca and Cr from (La,Ca)CrO₃ migrated into Ni–YSZ and (La,Sr)MnO₃ electrodes, forming dense regions within the electrodes and terminating the sintering of (La,Ca)CrO₃. Thermodynamic calculations (6) and powder mixing experiments (5, 7) indicated the possible formation of CaZrO₃, NiCr₂O₄, and La₂Zr₂O₇ as reaction products. In a postmortem examination of a Risø SOFC stack, we observed that a residual Ca–Cr–O liquid from sintered (La,Ca)CrO₃ migrated through the entire thickness of a Ni–YSZ anode (~100 μm) and reacted with the YSZ electrolyte.

It is possible that Ca may originate from other sources in addition to the Ca–Cr–O liquid. It may come from CaO which is a high temperature residue (>1400°C) in A-site excess (La,Ca)CrO₃ (8), and it is conceivable that Ca may be extracted from the (La,Ca)CrO₃ matrix.

This study examines the possible sources and the conditions under which Ca migration will occur during the fabrication and operation of SOFCs. The study focuses specifically on reactions of Ca with YSZ, since this SOFC material is the most seriously affected by the Ca migration.

2. EXPERIMENTAL

Calcium doped lanthanum chromite compositions were synthesized by drip pyrolysis (9) of an aqueous mixture of

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La, Ca, and Cr nitrates (Johnson Matthey Alfa Products) and glycine in a rotating tube furnace heated to 550°C. Six moles of glycine and 500 ml of distilled water were added per mole of final product. As-synthesized powders were calcined in air at 950°C for 8 h.

Compositions from the CaO–Cr₂O₃ phase system were prepared to compare their reactivities with YSZ. Calcium oxide (CaO) was obtained by calcining CaCO₃ (Johnson Matthey Alfa Products) in air at 1200°C for 2 h. Calcium chromate, CaCrO₄, was synthesized from the combustion of the Ca and Cr nitrates and glycine (10) followed by calcination in air at 800°C for 2 h. A Ca-rich two phase mixture, CaO–2CaCrO₄, was prepared by mixing CaCO₃ with CaCrO₄ and calcining in air at 800°C for 8 h. When this mixture was reheated to a temperature higher than 885°C, in a subsequent experiment, it was expected to form the compound Ca₃(CrO₄)₂.

A Ca-poor mixture (2CaCrO₄–Cr₂O₃) was made from Cr₂O₃ and CaCrO₄ and calcined under the same conditions as the Ca-rich composition. The spinel β-CaCr₂O₄ was expected to form in the 2CaCrO₄–Cr₂O₃ mixture when it was reheated at a temperature greater than 1022°C (3). This temperature is also the melting temperature of CaCrO₄. The latter two compositions were calcined at 800°C to avoid the melting of CaCrO₄, possibly causing phase segregation or altering the initial composition. The Cr₂O₃ (Baker) and YSZ (Tosoh-Zirconia TZ-8Y) powders were utilized as-received. Nominal purities of the raw materials were >99 at%.

Tape cast YSZ plates were prepared by in-house casting methods (11) and sintered at 1300°C for 6 h. The nominal plate thickness was 200 μm.

Reaction products were determined by heating mixtures of La_{0.76}Ca_{0.24}CrO₃ or CaCrO₄ and YSZ powders. The mixtures were ground in a mortar and pestle, pressed into pellets, and reacted at various times and temperatures as specified in Table 1. The reacted pellets were then crushed and examined by X-ray powder diffraction (XRD). Selected specimens were analyzed with a transmission electron microscope (TEM), equipped with an energy dispersive spectrometer (EDS).

The effect of Ca–Cr–O emanating from (La,Ca)CrO₃ was analyzed as a function of the sintering temperature. Specimens of La_{0.70}Ca_{0.36}CrO₃ were sintered in air for 2 h at 1300, 1450, and 1600°C on YSZ plates. The densities of the sintered pellets ranged between 90 and 95% of the theoretical values. Sintered pellets were washed in a 2 vol% HCl aqueous solution to dissolve the Ca–Cr–O residue on the surface, and then polished and placed on sintered YSZ plates. A pressure of ~4 kPa was applied by placing weights on each couple. The reaction couples were annealed at 1200°C in air for 100 h.

The relative reactivity of Ca–Cr–O to YSZ was determined by placing pelletized powders of CaO, CaO–

TABLE 1
Composition, Reaction Conditions, and Phase/Chemical Analysis of Mixed Powders

Composition mixed with YSZ	Molar ratio	Reaction conditions	Phase and chemical analysis
La _{0.76} Ca _{0.24} CrO ₃ + ~5 mol% CaCrO ₄	1:1	1000°C/100 h	XRD: LCC and YSZ TEM/EDS: Ca in YSZ, CaCrO ₄
La _{0.76} Ca _{0.24} CrO ₃ + ~5 mol% CaCrO ₄	1:1	1200°C/100 h	XRD: LCC and YSZ
CaCrO ₄	0.41:1	1200°C/100 h	XRD: YSZ and β-CaCr ₂ O ₄ TEM/EDS: CaCr ₂ O ₄ , Ca in YSZ CaZrO ₃
CaCrO ₄	1.36:1	1200°C/24 h	XRD: YSZ, CaCrO ₄ , β-CaCr ₂ O ₄ , CaZrO ₃ TEM/EDS: CaCr ₂ O ₄ , CaZrO ₃ , Ca in YSZ, CaCrO ₄ , Y–Cr–O

2CaCrO₄, CaCrO₄, 2CaCrO₄–Cr₂O₃, and Cr₂O₃ on YSZ plates and heating to 1200°C for 100 h or 1300°C for 2 h.

Reaction couples were embedded in epoxy, cut perpendicular to the interface, polished, and analyzed in a scanning electron microscope (SEM) equipped with EDS. A reaction depth was determined from SEM examinations by subtracting the narrowest span of the unreacted region from the total initial thickness of the plate (See Fig. 1).

3. RESULTS AND DISCUSSION

Calcium chromate is reported to exsolve out of (La,Ca)CrO₃ at 1000°C when the Ca substitution exceeds 25 at% (2). Remnants of this and similar phases in sintered (La,Ca)CrO₃ were found in the ensuing results to be the major source of Ca reaction when melting took place.

3.1. Powder Mixtures

Powder mixture experiments helped identify the reaction products and the extent of reaction of the Ca–Cr–O liquid phase with YSZ. Table 1 summarizes these results. Initially, XRD analysis of powder mixtures of La_{0.76}Ca_{0.24}CrO₃ + ~5 mol% exsolved CaCrO₄ and YSZ showed no apparent interaction. Only CaCrO₄ was observed to dissolve into La_{0.76}Ca_{0.24}CrO₃, but a reexamination of the powder with TEM and EDS revealed that YSZ particles contained dissolved Ca. Residual Ca–Cr–O particles were also identified within the reacted mixture.

Since the amount of Ca available for reaction with YSZ was limited in (La,Ca)CrO₃, mixtures of CaCrO₄ with YSZ

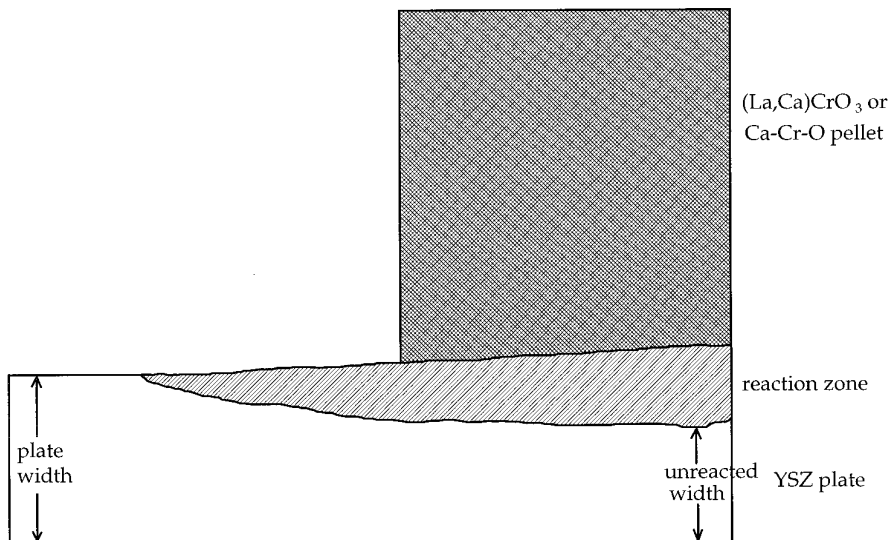


FIG. 1. A sketch of the reaction depth measurement. The reaction depth was calculated by subtracting the narrowest span of the unreacted region from the initial YSZ plate thickness.

were also studied. $CaCrO_4$ has nearly the same composition as the transient liquid phase in $(La,Ca)CrO_3$. The reaction products of the $CaCrO_4$ and YSZ mixture can be related to those of the transient liquid phase.

Equal volume fractions (0.41 molar ratio) of $CaCrO_4$ and YSZ powders reacted at $1200^\circ C$ for 100 h yielded β - $CaCr_2O_4$ and YSZ as shown in Fig. 2. TEM/EDS analy-

ses show that the extra Ca dissolved into YSZ and a small amount of $CaZrO_3$ was observed (Table 1). When the molar ratio of $CaCrO_4$ and YSZ was increased to 1.36, enough Ca was released to form $CaZrO_3$, thereby reducing the amount of YSZ (Fig. 3). According to TEM/EDS analyses, some yttrium is found to be soluble in $CaZrO_3$. However, it is observed that the Zr/Y ratio is lower for YSZ

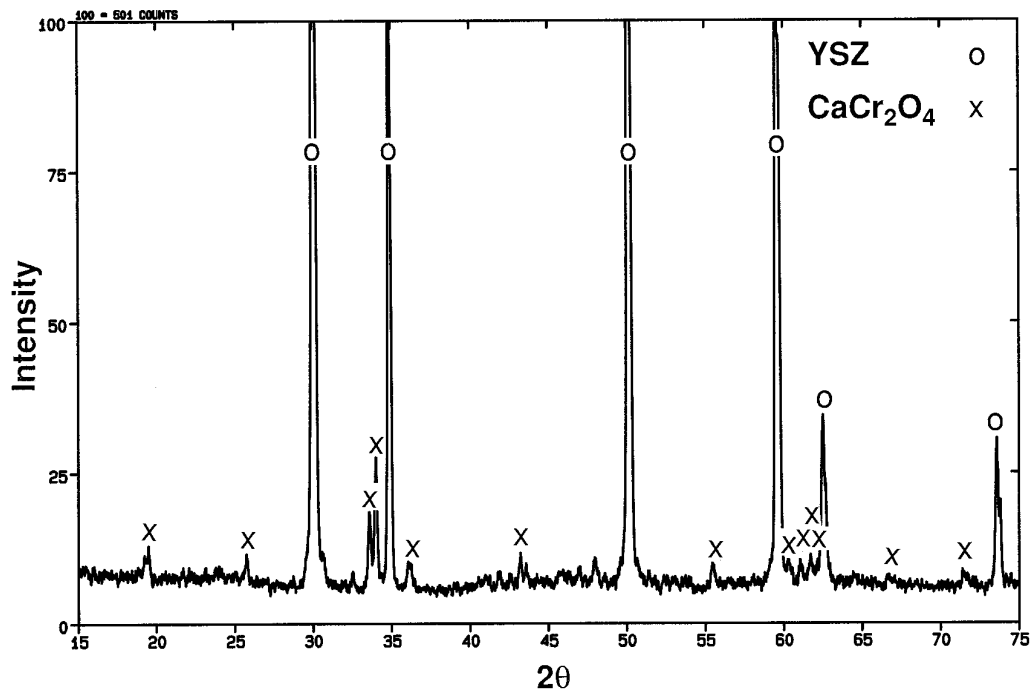


FIG. 2. XRD of a 0.41:1 molar ratio of $CaCrO_4$ and YSZ powders. Annealed at $1200^\circ C$ for 100 h.

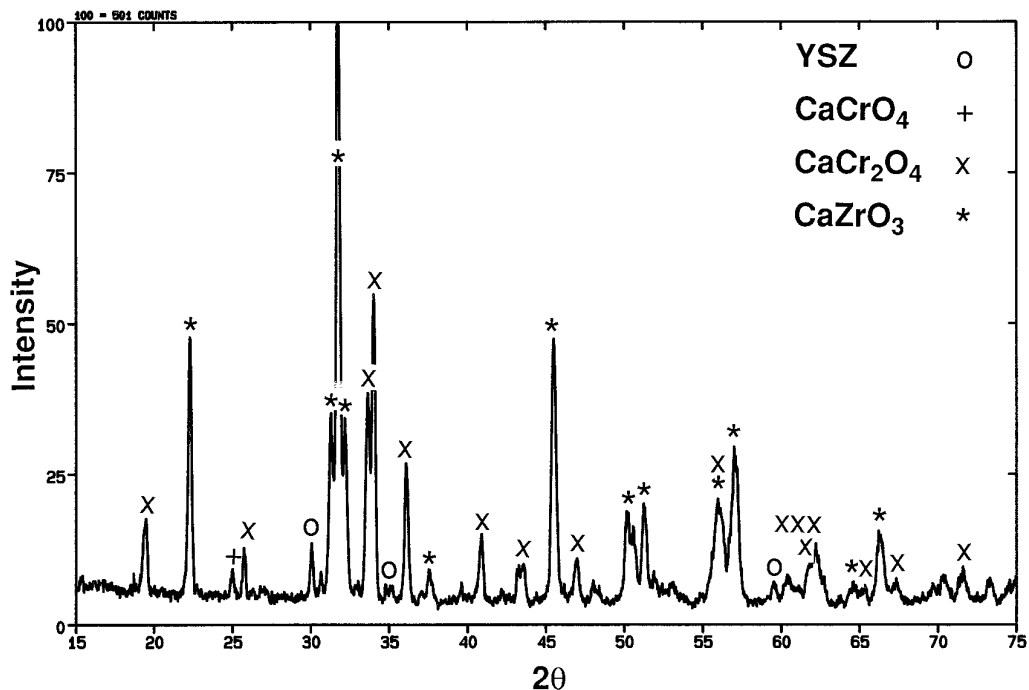
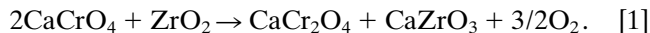


FIG. 3. XRD of a 1.36:1 molar ratio of CaCrO_4 and YSZ powders. Annealed at 1200°C for 100 h.

than for CaZrO_3 which indicates that most of the Y is concentrated in YSZ with respect to the CaZrO_3 phase. The TEM/EDS analyses of the powder with the molar ratio of 1.36 CaCrO_4 /YSZ also showed small amounts of CaO and an unidentified Y–Cr–O phase.

These results show that Ca is released from CaCrO_4 into YSZ until $\beta\text{-CaCr}_2\text{O}_4$ is formed. $\beta\text{-CaCr}_2\text{O}_4$ appears to be stable with respect to the release of Ca at high temperatures under these conditions. Calcium-rich Ca–Cr–O compositions which make up the transient liquid phase in (La,Ca) CrO_3 were also expected to yield the same reaction products. A simplified reaction at 1200°C may be written:



The reaction becomes more complicated due to the presence of Y in the ZrO_2 . An exact figure of the solubility of Ca in YSZ and an understanding of the final state of Y is needed to write a more complete reaction.

Nevertheless, Eq. [1] demonstrates the importance of developing (La,Ca) CrO_3 compositions which, after sintering, contain no residual CaCrO_4 or higher Ca content compositions, since they will react to form CaZrO_3 .

3.2. Ca–Cr–O on Sintered YSZ

The relative reactivities of the different Ca–Cr–O compositions became apparent when pellets of the compositions were set on YSZ plates, annealed, and then examined

by the SEM. Table 2 illustrates the effects of composition and liquid formation on the reactivity of Ca–Cr–O and YSZ. Measurements of the reaction depths demonstrate the degree of reaction.

The CaO and $2\text{CaCrO}_4\text{-Cr}_2\text{O}_3$ compositions reacted with YSZ only at points of contact with YSZ, and the Cr_2O_3 showed no traceable interaction.

Although the reactivity of CaO to YSZ is high, the overall reaction between the two materials was limited because it occurred by solid state diffusion through a few contact points. Reaction depths observed with the SEM and EDS were on the order of $1\ \mu\text{m}$. Similarly, residual

TABLE 2
Reaction Depth of Ca–Cr–O on Sintered YSZ Plates

Compound	Reaction depth (μm)	
	$1200^\circ\text{C}/100\ \text{h}$	$1300^\circ\text{C}/2\ \text{h}$
Cr_2O_3	0	^a
$2\text{CaCrO}_4\text{-Cr}_2\text{O}_3$	<5	10
CaCrO_4	>200 ^b	50
$\text{CaO-}2\text{CaCrO}_4$	~1	>180 ^b
CaO	~1	^a
$\text{La}_{0.70}\text{Ca}_{0.36}\text{CrO}_3$ (all sintering temperatures)	>200 ^b	^a

^a Experiment not performed.

^b Reacted through the thickness of the YSZ plate.

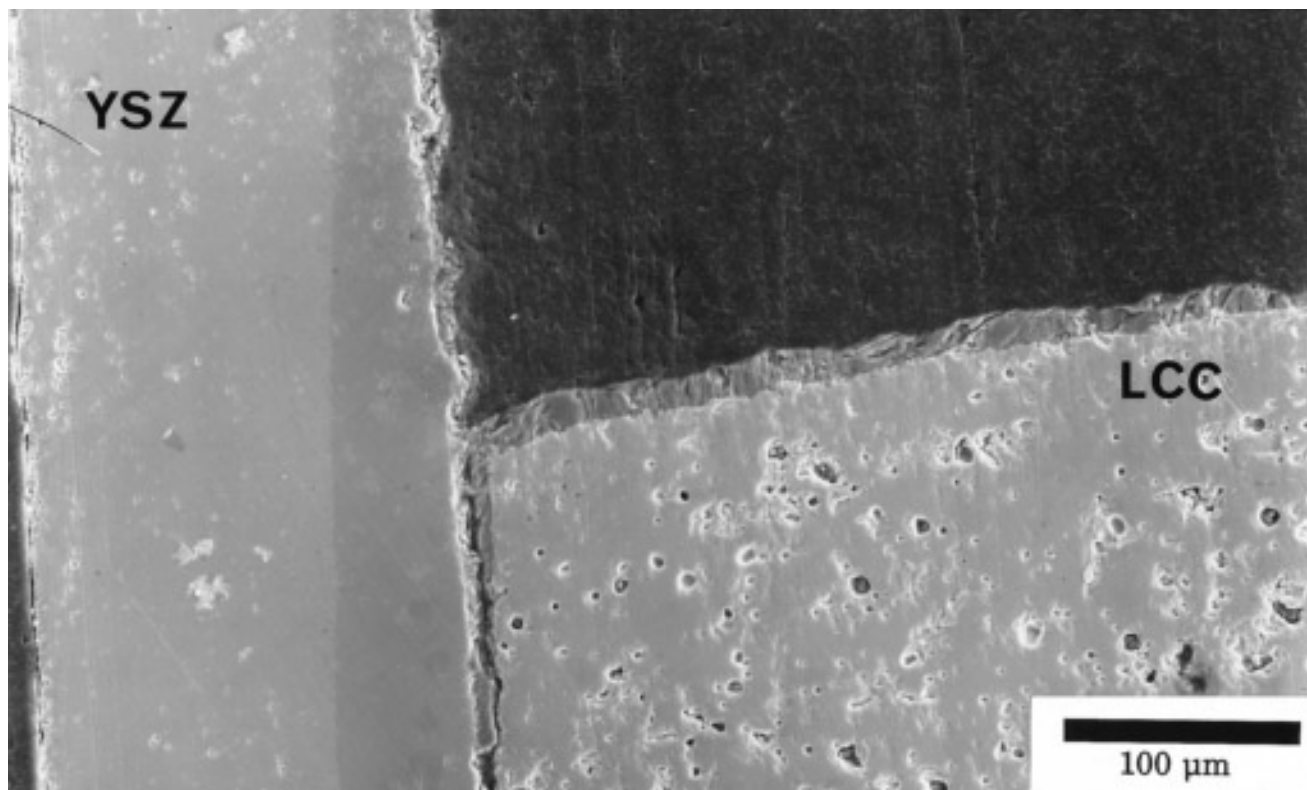


FIG. 4. SEM secondary electron image of La_{0.70}Ca_{0.36}CrO₃ (LCC) (sintered at 1300°C) on YSZ. Annealed at 1200°C for 100 h. The dark zone in YSZ contains Ca which has diffused into YSZ.

CaO on the surface of a (La,Ca)CrO₃ interconnect is expected to show limited overall reaction with YSZ because of the small percentage of contact area between CaO and YSZ.

The 2CaCrO₄-Cr₂O₃ mixture reacted because of the partial melting of CaCrO₄ in contact with the YSZ. However, further reaction was stopped due to the simultaneous formation of β-CaCr₂O₄ at the melting temperature. It is possible that a liquid phase would form at the dissociation of β-CaCr₂O₄ to CaCrO₄ during temperature cycling. However, on the (La,Ca)CrO₃ surface, this liquid would be only a small fraction of the total contact area.

The appearance of CaO or β-CaCr₂O₄ on the surface of (La,Ca)CrO₃ therefore plays a minor role in the overall reactivity of (La,Ca)CrO₃ with YSZ.

In contrast, the intermediate compositions, CaO-2CaCrO₄ and CaCrO₄, formed liquid phases which spread across and reacted with the YSZ surface. These two compositions displayed different behavior upon melting.

The CaCrO₄ melted incongruently, forming a mixture of a liquid and a solid. According to the CaO-Cr₂O₃ phase diagram (3), more than 80% of the CaCrO₄ was melted. The phase diagram also indicates that the amount of liquid in the mixture decreases with increasing Cr content. During the experiment, the liquid wet and spread in a thin layer

over the entire YSZ surface, leaving a skeletal form of the solid in the shape of the original pellet. Within the skeletal remains, needle shaped grains having a Ca/Cr ratio identical to that in β-CaCr₂O₄ were observed by SEM/EDS. These needle shaped grains were sometimes found embedded in remnants of the liquid phase. During the anneal at 1200°C for 100 h, the liquid phase from CaCrO₄ reacted through the thickness of the YSZ plate, but at 1300°C where the anneal time was only 2 h, the reaction reached a depth of 50 μm.

The CaO-2CaCrO₄ mixture at 1200°C showed very little interaction with YSZ, much like solid CaO, but when the temperature was increased to 1300°C, the pellet melted and reacted through the YSZ plate. Unlike CaCrO₄, this composition melted completely, losing the original form of the pellet. These observations are explained by the CaO-Cr₂O₃ phase diagram (3) which shows that Ca₃(CrO₄)₂ is solid at 1200°C, but is completely melted at 1300°C. At 1300°C the reaction depths of 2CaCrO₄-Cr₂O₃, CaCrO₄, and CaO-2CaCrO₄ are seen to increase with increasing Ca content.

These reaction depth measurements show that Ca is most reactive when it is in the form of a Ca-Cr-O liquid. Also, the overall reaction of the liquid phase increases as the Ca content increases.

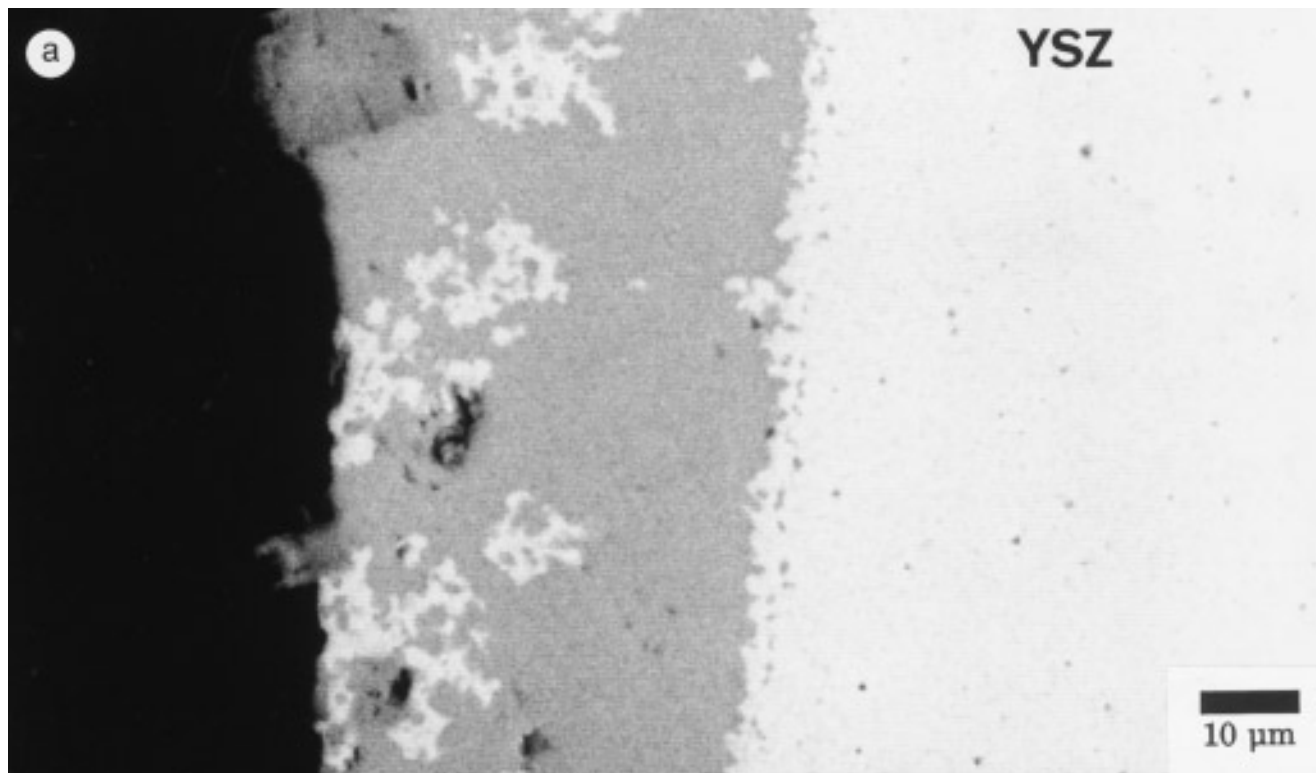


FIG. 5. SEM images of the Ca–Cr–O liquid–YSZ reaction at 1200°C for 100 h: (a) backscattered electron image; (b) CaK α X-ray mapping image; and (c) CrK α X-ray mapping image of the area shown in (a).

These results can be applied to the interaction of (La,Ca)CrO₃ and YSZ. Previous studies (1, 12) have reported that the Ca–Cr–O liquid phase in A-site excess (La,Ca)CrO₃ will increase in Ca content when equal parts of Ca and Cr, and O dissolve into the (La,Ca)CrO₃ matrix during the sintering process. Results from the present study suggest that the reactivity of the liquid phase will also increase during sintering.

3.3. Sintered (La,Ca)CrO₃ on Sintered YSZ

The reaction couples of sintered (La,Ca)CrO₃ and YSZ demonstrated that the presence of residual Ca–Cr–O liquid phase in (La,Ca)CrO₃ is the main cause of interaction.

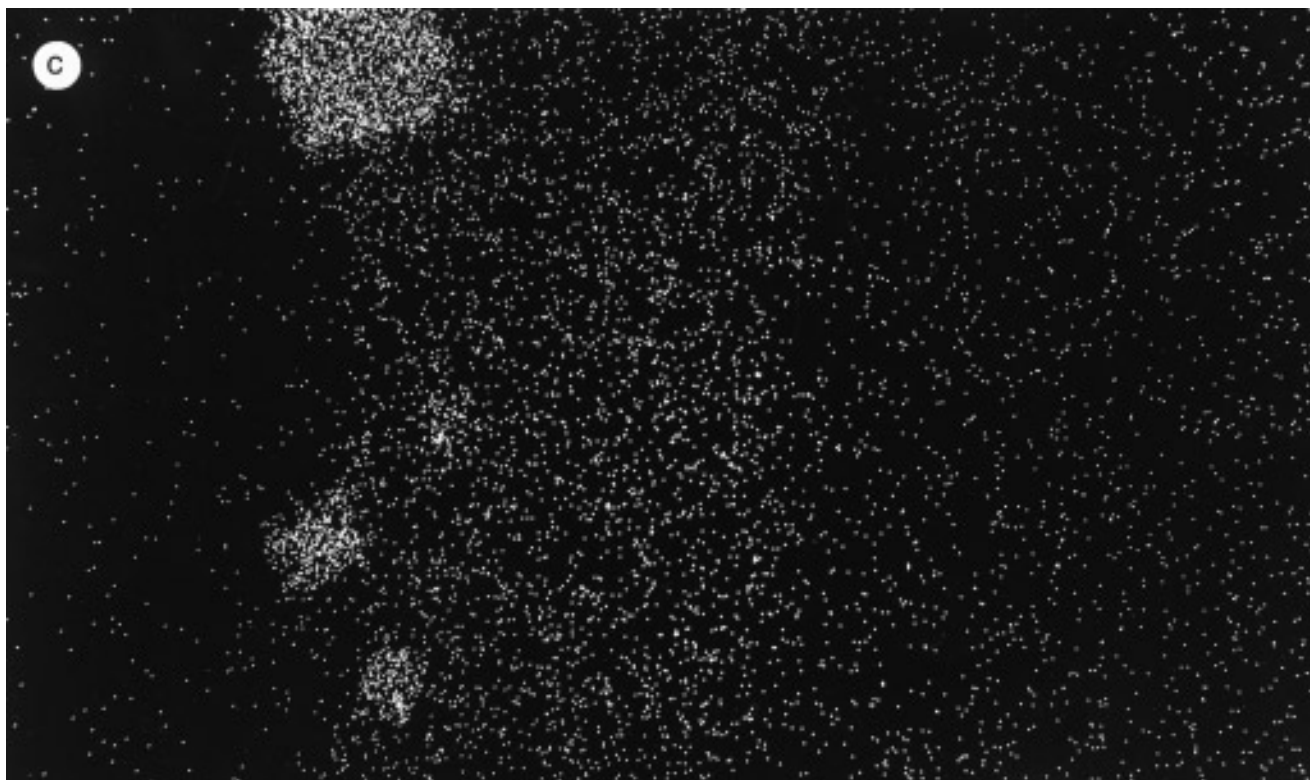
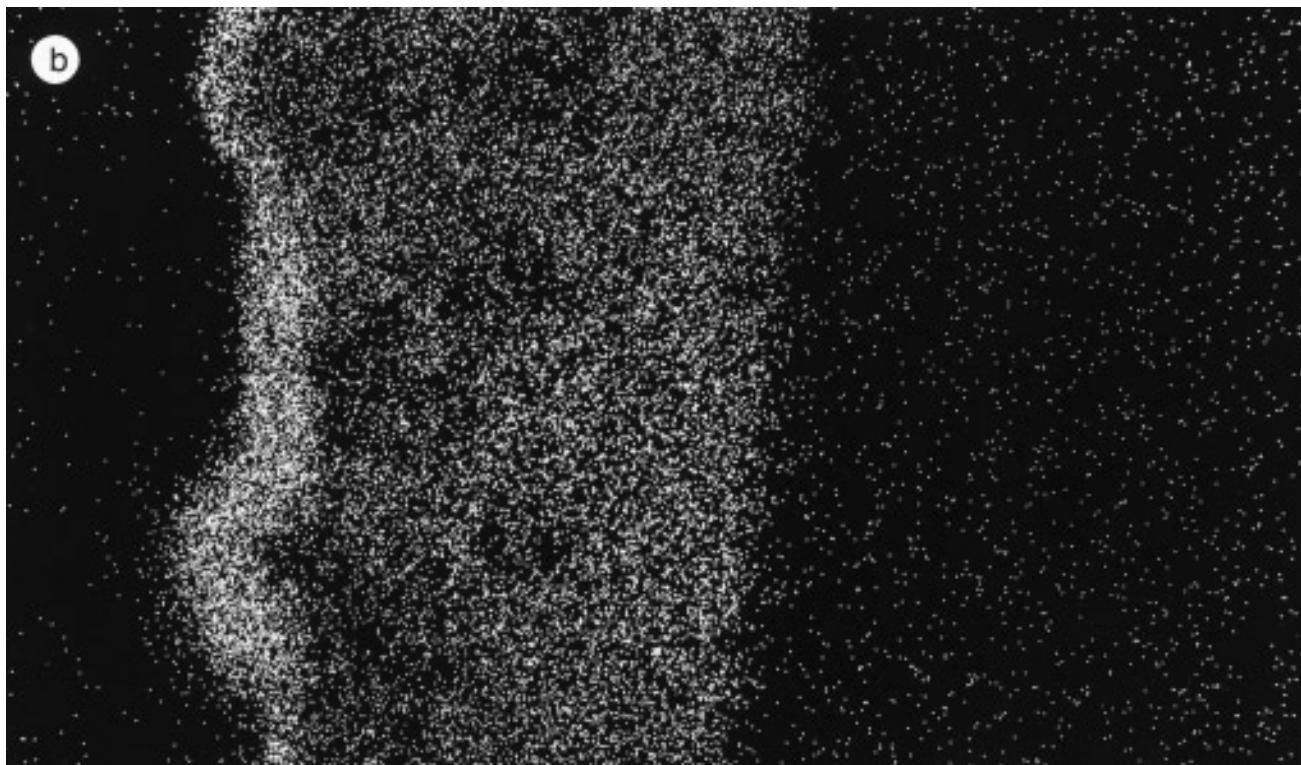
While sintering La_{0.70}Ca_{0.36}CrO₃ from 1300 to 1600°C, the reaction with the YSZ setter plate decreased with increasing temperature. Higher sintering temperatures decreased the volume of liquid phase as the solubility of Ca, Cr, and O increased in the chromite. However, each of these specimens reformed a Ca–Cr–O liquid which reacted through the thickness of the YSZ plate when they were annealed at 1200°C for 100 h.

Figure 4 is a SEM secondary image of a polished cross section of the La_{0.70}Ca_{0.36}CrO₃ (sintered at 1300°C)–YSZ reaction couple. The reaction region in the YSZ is identified as having a darker contrast to that of the uncontami-

nated YSZ. Elemental analysis of this region revealed equal atomic percentages of Ca and Zr, or CaZrO₃. The YSZ plate has expanded in the reaction region since CaZrO₃ has a lower density than YSZ.

In addition to the reaction region, a uniform 10 μ m layer can be seen in Fig. 4 on the free surfaces of the chromite and the YSZ. Spot EDS analyses showed that the layer on both the chromite and the YSZ contained only Ca.

Several trials performed in our lab and by others (1, 13) with similar (La,Ca)CrO₃ compositions (Ca = 24–36 at%) showed that a Ca–Cr–O residue is found on the free surface and in the grain boundaries of (La,Ca)CrO₃ after sintering at 1300–1400°C. It is possible that the dissolution rate of Ca, Cr, and O from the liquid into (La,Ca)CrO₃ was slow under sintering conditions and the residue was unable to completely dissolve into the (La,Ca)CrO₃ during the sintering time of 1–3 h. Similarly, during the first few hours of the 100 h anneal, residual Ca–Cr–O in the (La,Ca)CrO₃ grain boundaries melted again and exuded out at the free surface. A layer of Ca–Cr–O liquid formed on the (La,Ca)CrO₃ surface, overflowed onto the YSZ plate, and continued to spread and react along its surface. After a long time, Ca, Cr, and O were able to dissolve into the (La,Ca)CrO₃ bulk leaving excess CaO on its surface.

FIG. 5—*Continued*

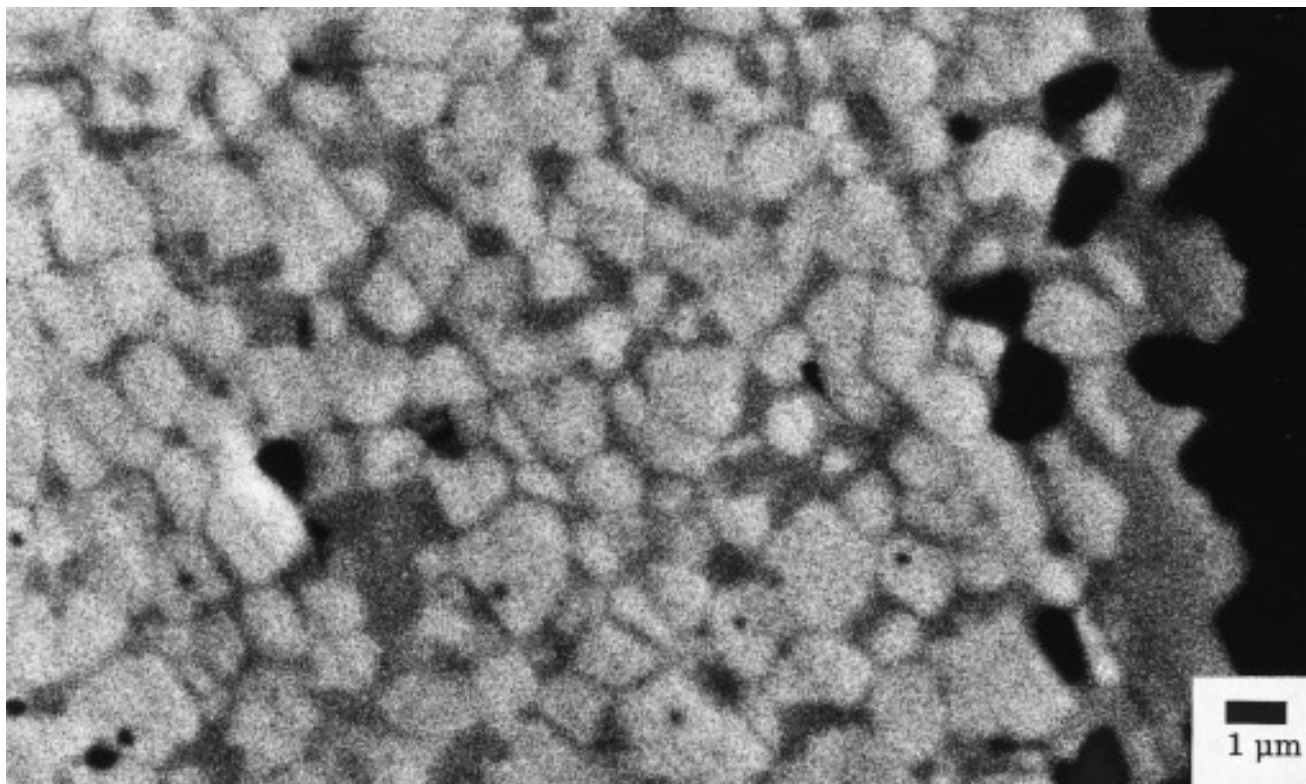


FIG. 6. SEM backscattered electron image of the YSZ–CaZrO₃ boundary (1200°C for 100 h). Dark areas are Ca-rich regions.

It is more difficult to understand why the uniform layer on the surface of YSZ contains only Ca. It was expected that the Ca would leach out of the liquid phase and leave a layer of β -CaCr₂O₄ on the surface. However, EDS analysis of the YSZ surface revealed unidentified grains scattered along the YSZ–liquid phase interface which were rich in Cr contained significant amounts of Y and some Ca and Zr (see also Fig. 5). These correspond to the Y–Cr–O grains identified by TEM/EDS of CaCrO₄ mixed with YSZ in the molar ratio 1.36:1 (Table 1). Apparently, Cr is more stable in this surface phase with Y than in β -CaCr₂O₄.

Figure 5 further illustrates the reaction behavior of the Ca–Cr–O liquid phase emanating from (La,Ca)CrO₃. (These SEM micrographs were taken from the same reaction couple shown in Fig. 4.) The reaction region is clearly evident in the backscatter electron image in Fig. 5a. The white region on the right side of the image is unreacted YSZ, whereas the gray region is the reaction zone, or CaZrO₃. Unreacted YSZ grains are seen within the reaction region. The darker gray Cr-rich grains can also be seen near the free surface. X-ray mapping of the elements shows the Ca-rich layer on the free surface and the extent of CaZrO₃ formation (Fig. 5b). It also shows the congregation of Cr into isolated grains (Fig. 5c).

A magnified view of the boundary between the YSZ

and the reaction region (Fig. 6) shows Ca enrichment along the grain boundaries of YSZ. (Darker areas define regions containing a higher concentration of lighter elements, such as Ca.) Here it is seen that CaZrO₃ forms preferentially in the grain boundaries of YSZ. This is probably due to a higher diffusion rate of Ca and O in the grain boundaries with respect to the bulk. The YSZ grains are subsequently digested in a growing CaZrO₃ matrix.

From the preceding results a reaction mechanism can be proposed. Initially, Ca and O from the liquid phase react with YSZ to form a CaZrO₃ layer. The Cr and Y segregate into a unidentified phase (possibly YCrO₃) with Ca and Zr which grows into equiaxed grains near the original free surface. The anomalous concentration of Y in this phase suggests that Y is soluble to some extent in CaZrO₃, and it can readily diffuse from YSZ through CaZrO₃ to form the unknown phase. Chromium is also sparingly soluble in CaZrO₃ (see X-ray dot map in Fig. 5c), but, since the driving force for the reaction of Cr with YSZ is small, most of the Cr migrates to the unknown phase.

Since the Ca–Cr–O liquid phase remnant remains in intimate contact with the YSZ plate, it continues to act as a reactive source of Ca for the formation of CaZrO₃. At the CaZrO₃/YSZ interface the reaction was seen to proceed preferentially along the YSZ grain boundaries.

4. CONCLUSIONS

A transient Ca–Cr–O liquid phase emanating from (La,Ca)CrO₃ is found to be the main cause of interaction between (La,Ca)CrO₃ and YSZ. The largest extent of reaction occurs upon melting and the reactivity of this melt increases with increasing Ca content. Compositions in which Ca exceeds the solubility limit of (La,Ca)CrO₃ were observed to continuously emanate the Ca–Cr–O liquid phase. This liquid phase reacts at the YSZ interface to form an intermediate layer of CaZrO₃. The CaZrO₃ layer reacts with YSZ along YSZ's grain boundaries, eventually digesting YSZ grains into a CaZrO₃ matrix. Cr and Y in the system were observed to combine into isolated grains along the original YSZ free surface.

These results emphasize the extreme difficulty of cosintering (La,Ca)CrO₃ with YSZ in the presence of a Ca–Cr–O liquid phase. They also show the need to eliminate the Ca–Cr–O liquid phase in sintered (La,Ca)CrO₃ to achieve compatibility with YSZ.

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