

Effect of processing on the microstructure and deformation of MgO-Al₂O₃, CaO-Al₂O₃, and SiO₂-Al₂O₃ layered composites

Chang Soo Kim and Stephen J. Lombardo

Department of Chemical Engineering, University of Missouri, Columbia, MO 65211

A process is developed whereby thin ceramic substrates layered with a coating are induced to adopt a different shape at elevated temperature without the application of external pressure. To achieve such deformation, thin beams of alumina are coated with magnesia, calcia, or silica; these composite beams are then heated to high temperature where deformation occurs. Scanning electron microscopy and compositional profiling indicate that for MgO and CaO coatings on alumina, a bilayer structure forms. For SiO₂ coatings on alumina, silicon is found throughout the substrate. A viscoelastic mechanics model based on strain mismatch in bilayer systems indicates how the curvature depends on the thickness of the two regions. A mechanistic model is presented that describes the strain mismatch in terms of the degree of conversion to a new phase, the amount of differential sintering between layers, and the amount of residual porosity present in the two layers of the substrate.

Key words: alumina, magnesia, layered composites, strain mismatch.

Introduction

In earlier work, we have developed a method to shape ceramic components *in situ* at high temperature, without the application of external stress. The method is based on applying a coating onto a substrate material and then heating the composite body to high temperature where deformation occurs. This method was first demonstrated for chromia coatings applied to alumina substrates [1, 2], and was then later extended to magnesia coatings on alumina substrates [3-6]. These two coating systems have a number of advantages for evaluating deformation behavior. For chromia coatings on alumina substrates, no new phases form, and it was concluded that the driving force for deformation was strain mismatch arising from the substitution of larger chromium cations for aluminum in the corundum structure. A large disadvantage of this system, however, was that chromia is quite volatile and thus contaminates the furnace.

For this reason, magnesia coatings on alumina were investigated. Large deformation was again observed, and spatially resolved X-ray diffraction [5] indicated that a spinel was formed as a new phase as a consequence of the magnesia coating penetrating into and reacting with the alumina substrate. The driving force for deformation in this system was thus attributed to formation of a new phase coupled with strain mismatch arising from differential sintering. Even though large

deformation was obtained, cracking at the interface was occasionally observed. We also note that for the magnesia-alumina system, as well as for the chromia-alumina system, no eutectic temperatures are traversed during the heating schedules to temperatures of 1400-1700 °C, and thus no liquid is present during the forming process.

In this work, we compare and contrast the deformation behavior and microstructural evolution of magnesia coatings on alumina with calcia and silica coatings on alumina. These latter two systems offer a number of pronounced differences to the systems examined earlier, namely in the complexity of their phase diagrams and in the possibility for the presence of liquid formation as a consequence of eutectic temperatures in the range of 1400-1700 °C. In addition, examination of these two new systems allows for the testing of the applicability of strain mismatch mechanics models and mechanisms evaluated earlier for chromia and magnesia coatings on alumina. Such understanding may also help in evaluating the mechanics and mechanisms accompanying deformation in other layered and composites systems, such as multilayer ceramic capacitors, low temperature co-fired ceramics, functionally graded materials, and fuel cells.

Experimental

A schematic of the processing route used to induce curvature into flat substrates is shown in Fig. 1. Green alumina substrates (Alcoa A-16, Bauxite, AR) were first prepared by tape casting as was reported in earlier work [3-6]. The dried substrates were next cut into beam specimens of 40 mm length × 3.0 mm width for

*Corresponding author:
Tel : 573-884-1644
Fax: 573-884-4940
E-mail: lombardos@missouri.edu

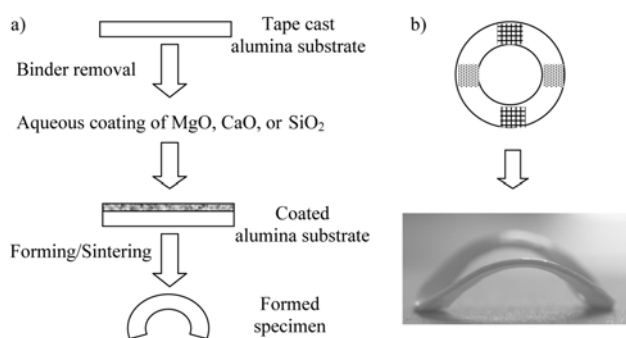


Fig. 1. a) Schematic of the processing method used to introduce curvature into a flat substrate. b) Example of a wave spring formed by applying a SiO_2 coating on a green alumina substrate in an alternating top and bottom fashion (see shaded regions) at 90° intervals. The wave spring is 2.5 cm in diameter.

different thicknesses between 0.8 and 3 mm. The binder was removed in a box furnace in air with a heating cycle of a ramp of 2 K minute^{-1} to 400°C for a 4 h hold, followed by a ramp of 2 K minute^{-1} to 800°C for 6 h hold, and then a controlled cooling at 10 K minute^{-1} to room temperature.

To coat the substrates, water-based slurries of the coating materials were prepared by the same method as was used in earlier work [5, 6]. The coatings evaluated were MgO (Aldrich, St. Louis, MO, -325 mesh), CaO (Fisher, Fairlawn, NJ), and SiO_2 (Aldrich, Milwaukee, WI, -325 mesh). After the coating was dried, the substrates with the coated side on top were heated in a box furnace in air and then cooled at 10 K minute^{-1} to room temperature. An example of a ceramic wave spring fabricated by coating SiO_2 on alumina is shown in Fig. 1.

After cooling, the curvature of the substrates was determined. The microstructure of the samples was analyzed by scanning electron microscopy (SEM, AMRAY 1600) and energy dispersive X-ray spectroscopy (EDS). For these two analyses, samples were mounted in epoxy, polished, and then carbon coated. To obtain grain size and shape information, selected samples were thermally etched. For the EDS analysis, quantitative compositions were determined using oxide standards and using Castaing's approximation and the atomic number/absorption/fluorescence (ZAF) method, as reported earlier [6].

Results and Discussion

Effect of Processing Conditions

The degree of deformation is expected to depend on a number of processing parameters, including the amount of coating applied on the green substrates and the amount of coating incorporated into the substrate at high temperature, *i.e.*, the coating uptake. In Fig. 2a is shown the coating uptake on the alumina substrate as a function of the amount of coating applied to the green substrates. For SiO_2 and MgO coated on Al_2O_3 , the

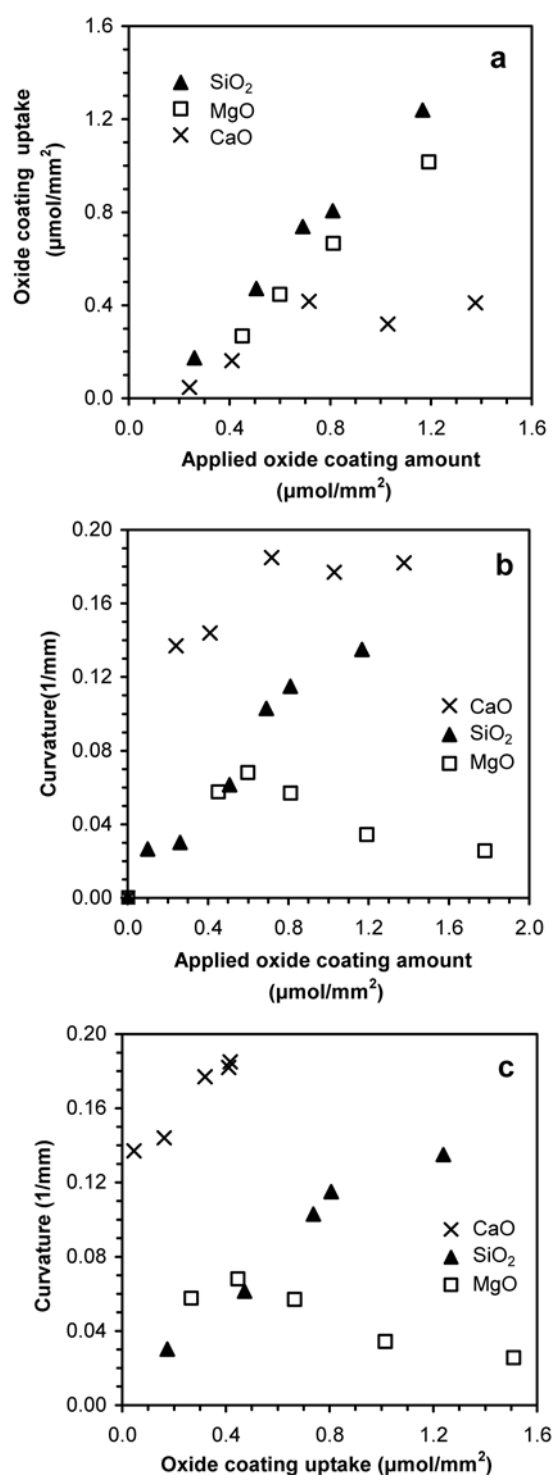


Fig. 2 a) Oxide coating uptake versus amount of applied coating of MgO, CaO, and SiO_2 on green alumina substrates held at 1600°C for 4 h. b) Curvature versus amount of applied coating of MgO, CaO, and SiO_2 on green alumina substrates held at 1600°C for 4 h. c) Curvature versus amount of uptake of MgO, CaO, and SiO_2 on green alumina substrates held at 1600°C for 4 h. For all substrates, the original thickness was 0.8 mm.

coating uptake after heating to 1600°C for 4 h varies nearly linearly with applied coating, and thus the applied amount is essentially all incorporated into the

substrate. For CaO as the coating material, the coating uptake after heating to high temperature first increases with applied coating and then approaches a plateau region. The plateau occurs because only a limited amount of the coating is incorporated into the substrate and the remainder is not strongly adherent to the substrate after the heating cycle.

In Fig. 2b is shown how the curvature varies with the amount of applied coating in the green state. For all three coatings, the curvature first increases with increasing amount of applied coating. For MgO and CaO coatings, a maximum or plateau amount of curvature is reached. For the SiO₂ coatings, however, no maximum or plateau in curvature is observed over the range of coatings examined here. The largest curvature in each system increases in the order of coating material as CaO>SiO₂>MgO and this ordering occurs over a range of applied coating amounts.

Figure 2c illustrates how the curvature of the substrates varies with coating uptake after heating to high temperature. For CaO as the coating material, the maximum amount of curvature coincides with the saturation of the coating uptake. For MgO as the coating material, the maximum curvature corresponds to a specific amount of applied coating, and hence coating uptake. For SiO₂ as the coating, no maximum or saturation curvature is observed over the range of coating examined here. For higher coating amounts of SiO₂ beyond what is shown here, delamination occurred, and thus the coatings were no longer in uniform contact with the substrates.

The next processing variable to be investigated was the effect of hold temperature on the degree of curvature for a fixed amount of applied coating corresponding to the largest amount of curvature in each system. Figure 3 shows that with increasing temperature of the 4 h hold period, the curvature of the substrates increases for each coating material. The difference in curvature among the coatings is small at 1300-1400 °C, and increases strongly above 1500 °C. For the higher temperatures, the curvature increases in the order of coating material as CaO>SiO₂>MgO.

The curvatures observed in Figs. 2 and 3 are quite large for all of the coatings applied to green substrates. It is thus of interest to know how the density of the substrates influences the amount of curvature. Figure 4 shows how the curvature varies with hold temperature and coating material for samples coated in the dense state, *i.e.*, the samples had been pre-densified by heating to 1600 °C for 4 h. The curvature for samples coated in the dense state is typically 10-30% of the curvature observed for samples coated in the green state. At 1600 °C and above, the ordering of the curvature with type of coating material is nearly the same as was observed in Fig. 3 for samples coated in the green state. The temperature at which the dense substrates begin to deform appreciably, however, is higher as

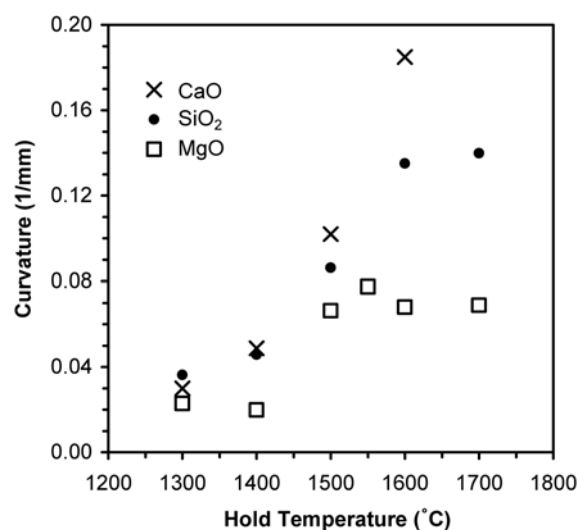


Fig. 3. Curvature of MgO, CaO, and SiO₂ coated green alumina substrates held at different temperatures for 4 h. The coatings were applied at an amount corresponding to the maximum curvature. The original substrate thickness was 0.8 mm.

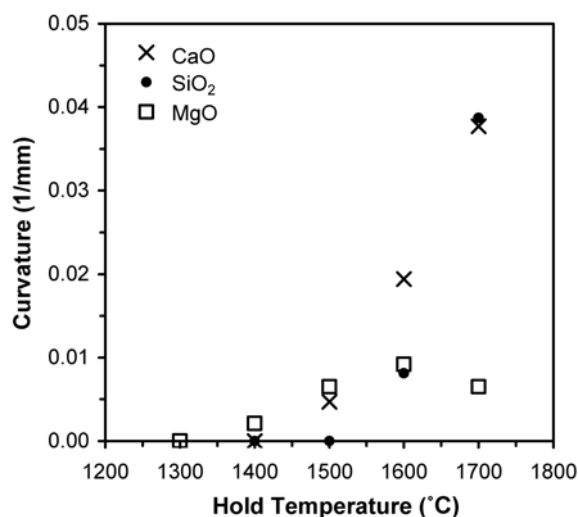


Fig. 4. Curvature of MgO, CaO, and SiO₂ coated dense alumina substrates held at different temperatures for 4 h. The coatings were applied at an amount corresponding to maximum curvature. The original substrate thickness was 0.8 mm.

compared to the temperature at which the green substrates begin to deform (see Fig. 3). Because the curvature is much lower for coatings applied to dense substrates as compared to green substrates, we will focus on the behavior of green substrates for the balance of this paper.

The effects of substrate thickness and coating type on the curvature are shown in Fig. 5 for samples held at 1600 °C for 4 h. With increasing thickness, the curvature decreases rapidly. For the thinnest substrates of 0.8 mm original thickness, the amount of deformation increases in the order of coating material as CaO>SiO₂>MgO. For the thicker substrates, the difference in curvature among the different coatings becomes small,

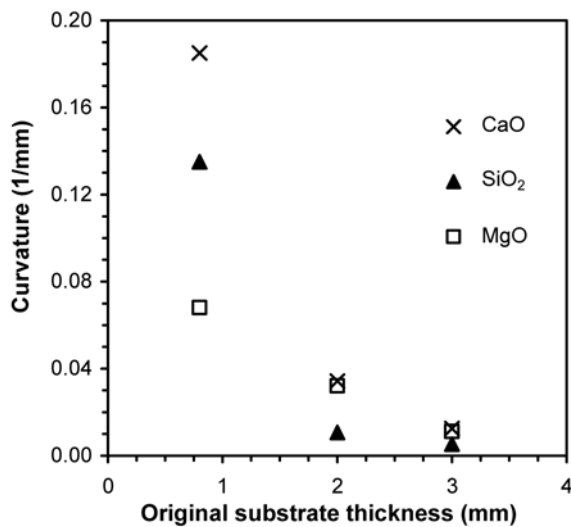


Fig. 5. Curvature versus substrate thickness for MgO, CaO, and SiO₂ coated green alumina substrates held at 1600 °C for 4 h. The coatings were applied at an amount corresponding to maximum curvature.

and the substrates coated with SiO₂ now exhibit the smallest amount of deformation.

Concentration Profiles and Microstructure

The processing temperature is expected to influence the interaction between the coating and the alumina substrate, and both penetration of the coating material into and reaction with the substrate are possibilities. Figures 6a-c illustrate the degree of penetration of the cations from the MgO, CaO, and SiO₂ coatings into the substrates as a function of temperature for a 4 h hold. For substrates coated with MgO, the EDS data in Fig. 6a show that the depth of Mg cation penetration increases with increasing temperature. More detailed analysis of this system in previous work [6] has led to the conclusion that the outermost region of the substrate has a plateau MgO/Al₂O₃ molar ratio of 0.65 ± 0.1 , which may correspond to a mixture of spinel and alumina or to a MgO-deficient spinel-type structure [7, 8]. The presence of spinel was also verified by spatially resolved X-ray diffraction [5].

Figure 7 shows micrographs of samples coated with MgO and then held at 1600 °C for 4 h. Figure 7a shows that on the top surface of the substrate, porous remnants of the coating are evident. Below this, a denser region, denoted as h_1 , is observed which extends approximately 80 μm into the sample; this distance is consistent with the depth of Mg penetration from EDS profiling in Fig. 6a. Below the h_1 region is a slightly more porous region, denoted as h_2 , which corresponds to the balance of the thickness of the substrate. Figure 7b is a higher magnification micrograph of the interfacial region in Fig. 7a between h_1 and h_2 . The h_2 portion of the substrate has remained primarily as pure Al₂O₃ and exhibits a characteristic Al₂O₃ microstructure with angular grains of 2-3 μm average size and some intergranular

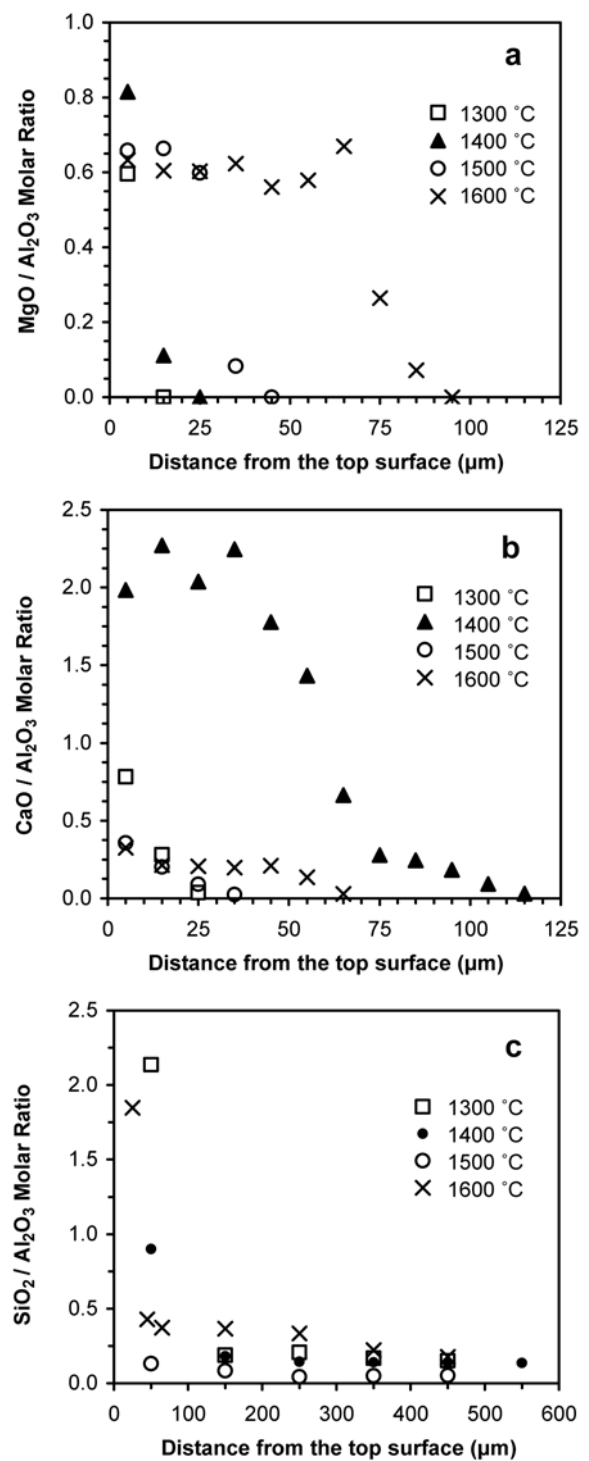


Fig. 6. Concentration profiles, as determined by EDS, with depth for green substrates coated with a) MgO, b) CaO, and c) SiO₂ and held at different temperatures for 4 h.

porosity. The h_1 region of the substrate, which contains appreciable MgO has less porosity. This porosity, however, is spherical in shape and is primarily intragranular, and presumably arises during the recrystallization to spinel. Although not easily seen in Fig. 7b, the grains in the h_1 region are 10-20 μm in size.

The depth of cation penetration for substrates coated

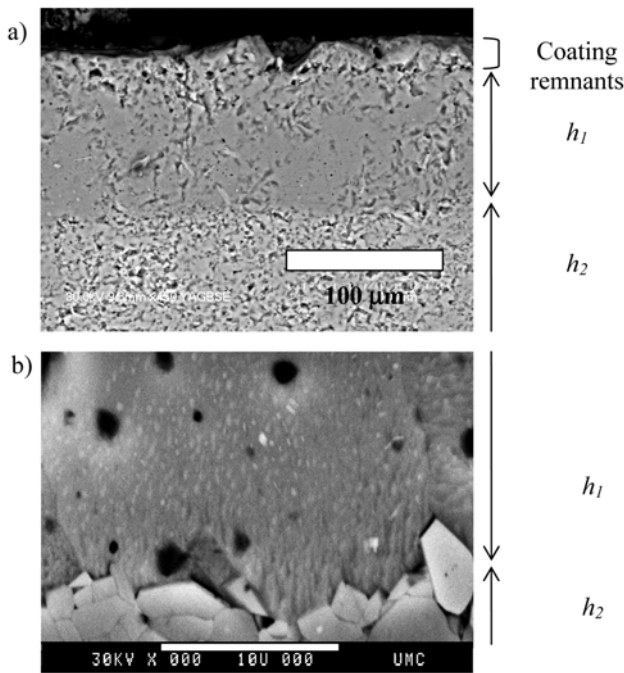


Fig. 7. SEM micrographs for MgO coated alumina substrates held at 1600 °C for 4 h. a) Two regions, denoted as h_1 and h_2 , are evident along with remnants of the coating on the top surface. b) Interfacial region between the h_1 and h_2 regions.

with CaO is shown in Fig. 6b. With the exception of the substrates held at 1400 °C, the depth of penetration of Ca increases with increasing temperature. We note that for the 1400 °C data in Fig. 6b, the outer portion of the substrate is at a CaO (C)/ Al_2O_3 (A) molar ratio of approximately 2, which corresponds to the phase field bounded by the CA and C_3A compositions [9]. This phase field corresponds to the lowest eutectic temperature of 1371 °C for the $\text{CaO-Al}_2\text{O}_3$ system. The presence of liquid may thus facilitate much further penetration of calcium into the substrate. Beyond 70 μm , the $\text{CaO/Al}_2\text{O}_3$ molar ratio approaches the plateau value of 0.17; this ratio is also strongly evident for the substrates held at the 1600 °C and corresponds to the phase field of the CA_2 and CA_6 compositions, and is in fact almost on the stoichiometric CA_6 composition [9-13]. This progression in composition towards the alumina-rich side of the phase diagram coincides with an increase in the eutectic temperature from 1371 °C to 1775 °C.

Figures 8a and 8b show the microstructures of substrates coated with CaO which were held at 1600 °C and 1500 °C for 4 h, respectively. Remnants of the coating remain on the surfaces of the substrates, and two regions denoted as h_1 and h_2 are also evident, as was observed in Fig. 7a. Figure 8c is a higher magnification micrograph of the interfacial region in Fig. 8a between the h_1 and h_2 regions. Within the interfacial region, two types of grains are apparent. The light, more angular grains are similar in shape and size to the pure Al_2O_3 grains in Fig. 7b. The darker second type of

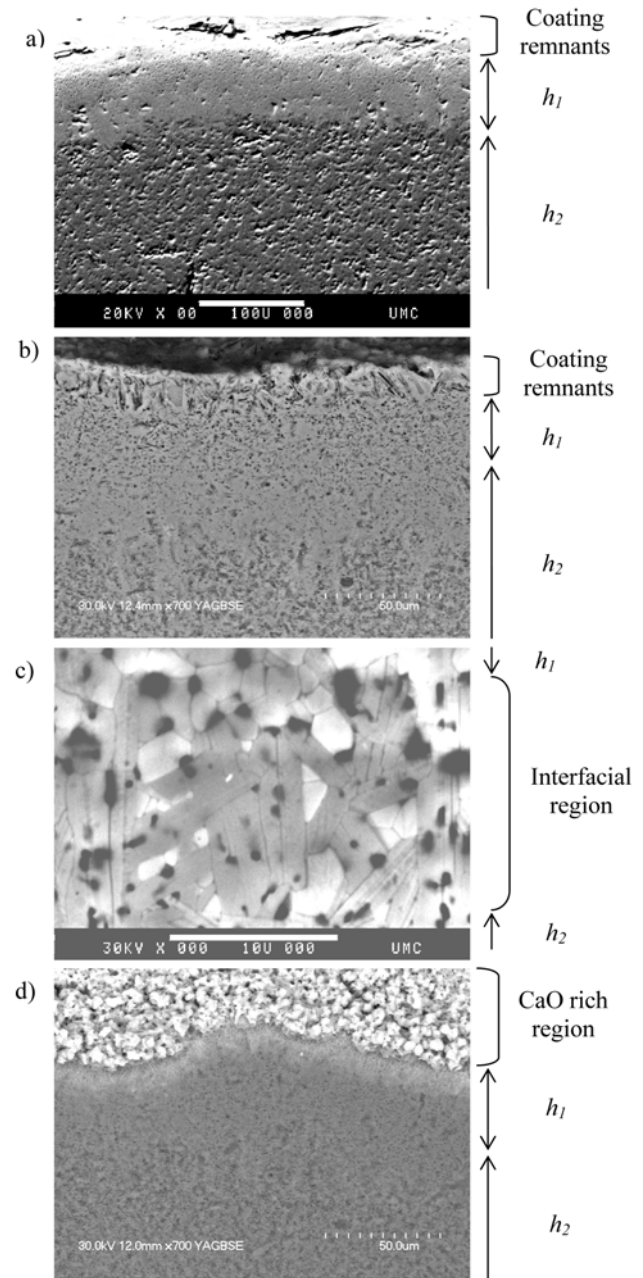


Fig. 8. SEM micrographs of CaO coated alumina substrates held at different temperatures for 4 h at a) 1600 °C; b) 1500 °C; c) 1600 °C; and d) 1400 °C.

grain is larger with a plate-like grain shape; this has been referred to in the literature as the CA_6 microstructure [10-13]. The difference in porosity between the regions h_1 and h_2 appears to be small, but this is difficult to ascertain because of the grain morphology.

To explain the anomalous concentration behavior of Ca penetration for the $\text{CaO-Al}_2\text{O}_3$ system in Fig. 6b, the microstructures in Figs. 8b and 8d are helpful. For the sample held at 1400 °C, the coarse region in Fig. 8d corresponds to the high molar ratio of $\text{CaO/Al}_2\text{O}_3=2$ from EDS (see Fig. 6b) and extends about 70 μm into the sample. This molar ratio corresponds to the $\text{CA-C}_3\text{A}$ phase field. The coarse region is separated from

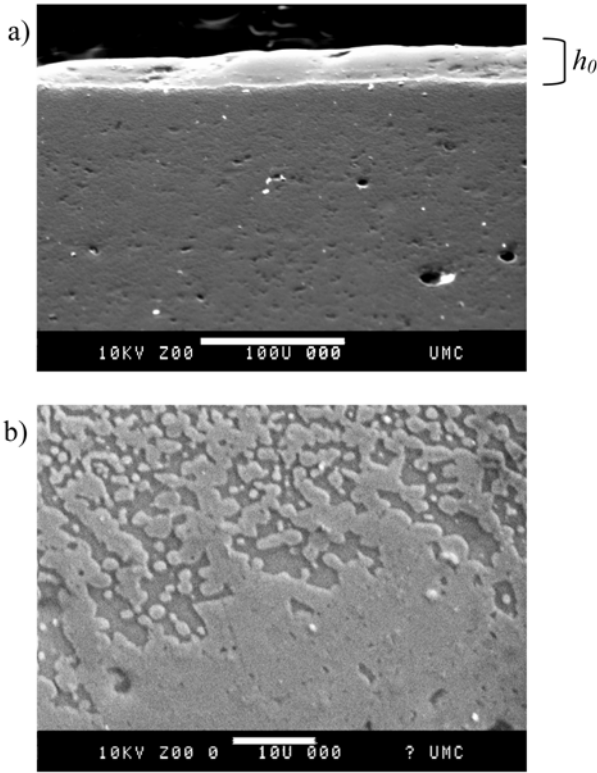


Fig. 9. a) SEM micrograph of a SiO₂ coated alumina substrate held at 1600 °C for 4 h. b) High magnification SEM image of the region 70 μm below the top surface of the substrate.

the bulk of the sample by a thinner region, which corresponds to the region of CaO/Al₂O₃ <0.25. The microstructure of this thin transition region in Fig. 8d is similar to that of the h_1 region in Fig. 8b for a substrate held at 1500 °C for 4 h. It may be that for the sample held at 1500 °C, the heating schedule is such that the reaction proceeds to a product on the Al₂O₃ rich side of the phase diagram, where the eutectic temperatures are higher, as compared to the CaO rich composition evident in Figs. 6b and 8d.

For substrates prepared with SiO₂ as the coating material, the depth of cation penetration versus hold temperature is shown in Fig. 6c. One notable difference is observed relative to the behavior of Mg and Ca cations in Figs. 6a and 6b, respectively. Silicon is seen to penetrate deep into the substrates, and except for the outer 50 μm, Si was observed through the entire thickness of the samples at a molar ratio of approximately 0.24, which corresponds to the silica-mullite two-phase field [14].

Figure 9 shows micrographs of samples prepared from the SiO₂-Al₂O₃ system and held at 1600 °C for 4 h. The topmost region of the substrate, denoted as h_0 in Fig. 9a, is 30 μm thick, is strongly adherent to the substrate, and has an amorphous appearance. The EDS data in Fig. 6c yields a SiO₂ rich composition for this topmost layer, which places it in the phase diagram where the eutectic temperature is below the hold

temperature, and thus liquid may be present. Below the SiO₂ rich region, the microstructure at low magnification appears fairly uniform, and no strong demarcation line exists in the balance of the thickness of the substrate. Figure 9b is a higher magnification micrograph of the substrate region below h_0 . Based on EDS analysis, the portion of the sample nearest the applied SiO₂ coating exhibits a two-phase microstructure with regions of Al₂O₃-rich grains bounded by pools rich in SiO₂. No porosity is evident in this region. Below the two-phase region, a very uniform microstructure is observed, which also appears low in porosity.

To summarize the concentration versus depth behavior, although each of the coatings differ in some specifics in how they are distributed in the substrates as a function of temperature, at 1600 °C, all three of the coating systems exhibit a plateau in the molar ratio of coating cation to Al₂O₃; this behavior is clearly indicated in Fig. 6. For the case of MgO as the coating, where a plateau molar ratio of 0.65 ± 0.1 MgO/Al₂O₃ is observed, X-ray diffraction in earlier work [5] clearly showed the existence of the spinel phase. For CaO as the coating, the plateau ratio of 0.17 ± 0.05 CaO/Al₂O₃ corresponds to a composition very near the CA₆ composition. For both MgO and CaO coatings, the existence of a region of constant composition in the substrates can be explained by a process governed by reaction control, as compared to diffusion control [15]. For SiO₂ coated substrates heated to 1600 °C, silicon is present throughout the substrate, which may arise because the sample is above the eutectic temperature. Upon cooling, the sample may exhibit the presence of silica, alumina, or mullite, depending to what extent reactions occur.

Deformation Mechanics and Mechanism

For substrates formed with MgO and CaO coatings, the microstructures and the plateau regions in the composition profiles suggest a bilayer structure of thicknesses h_1 and h_2 . Because the underlying alumina substrate behaves viscoelastically at the temperatures under consideration here [16-22], we can use the well known result to describe the curvature rate, $\dot{\kappa}$, of a bilayer structure as [20]:

$$\dot{\kappa} = \frac{6 \left(\frac{\eta_1}{\eta_2} \right) \left(\frac{1}{h_2} \right) \left(\frac{h_1}{h_2} \right) \left(\frac{h_1}{h_2} + 1 \right)}{\left(\frac{\eta_1}{\eta_2} \right)^2 \left(\frac{h_1}{h_2} \right)^4 + \left(\frac{\eta_1}{\eta_2} \right) \left(\frac{h_1}{h_2} \right) \left[4 \left(\frac{h_1}{h_2} \right)^2 + 6 \left(\frac{h_1}{h_2} \right) + 4 \right] + 1} \dot{D} \quad (1)$$

where $\dot{D}$ is the strain rate, η_i is the viscosity of the i th layer and h_i is the thickness. To obtain the net curvature, Eq. (1) can be integrated with respect to time when the temporal evolution of η_1/η_2 , h_1/h_2 and $\dot{D}$ is known. In the absence of such dynamic data, we can evaluate these quantities at their mean (constant) values to obtain the net curvature as:

$$\kappa = \frac{6\left(\frac{\eta_1}{\eta_2}\right)\left(\frac{1}{h_2}\right)\left(\frac{h_1}{h_2}\right)\left(\frac{h_1}{h_2}+1\right)}{\left(\frac{\eta_1}{\eta_2}\right)^2\left(\frac{h_1}{h_2}\right)^4 + \left(\frac{\eta_1}{\eta_2}\right)\left(\frac{h_1}{h_2}\right)\left[4\left(\frac{h_1}{h_2}\right)^2 + 6\left(\frac{h_1}{h_2}\right) + 4\right] + 1} D \quad (2)$$

To facilitate comparison of the curvature data, we define a dimensionless viscosity ratio, $\lambda = \eta_1/\eta_2$, a dimensionless thickness ratio, $\beta = h_1/h_2$, and a dimensionless curvature, $\gamma = h_2\kappa/D$, which leads to:

$$\gamma = \frac{6\lambda\beta(\beta+1)}{\lambda^2\beta^4 + \lambda\beta(4\beta^4 + 6\beta + 4) + 1} \quad (3)$$

The value of h_1 via β in Eq. (3) was determined by EDS profiling of the degree of cation penetration into the sample, and h_2 was calculated by the difference between the measured thickness of the sample and h_1 . Remnants of the coating on the substrate were not included in the determination of h_1 . The viscosity ratio, λ , and strain mismatch, D , were then obtained by nonlinear regression and are given in Table 1. For the samples fabricated in this work from MgO and CaO coatings, D ranges from 0.072-0.21, λ ranges from 1.0-4.4, and the regression coefficients, R^2 , range from 0.87-0.89. Figure 10 shows the dimensionless curvature versus layer thickness ratio for samples held at 1600 °C for 4 h. For both the MgO and CaO coatings, the curvature varies with the thickness ratio. The model predictions are also shown in Fig. 10, and we see that the model accounts for the strong effect of overall sample thickness on curvature seen in Fig. 5. In spite of the simplification invoked to obtain Eqs. (2) and (3), evaluating the deformation mechanics in terms of an analytical model probably does provide qualitative and some semi-quantitative insight into some of the important parameters governing the deformation process.

The values of λ in Table 1 obtained from regression analysis for the different coatings can be explained in the following manner. For MgO coatings on Al₂O₃, the value of $\lambda=4.4$ suggests that the viscosity of the top layer during deformation is much larger than that of the substrate. In the case of CaO coatings on Al₂O₃, the lower value of $\lambda=1.0$ as compared to that for MgO coatings on Al₂O₃ may indicate the presence of some transient liquid during the course of deformation. Although the presence of liquid is possible at 1600 °C, the final composition determined by EDS suggests that the eutectic temperature is above 1600 °C, and thus no

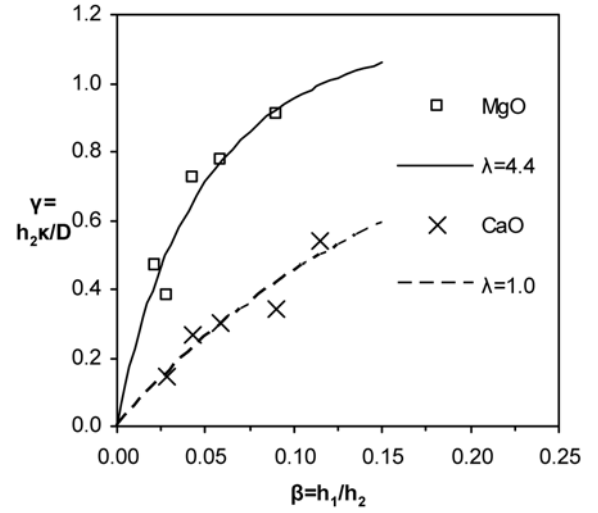


Fig. 10. Dimensionless curvature versus thickness ratio for alumina substrates coated with MgO or CaO and held at 1600 °C for 4 h. The symbols represent the results for the two coatings and the lines are from regression analysis using Eq. (3).

liquid should be present; this is consistent with the appearance of the microstructures in Fig. 8.

To explain the values for the magnitude of the strain mismatch in Table 1, different mechanisms may be postulated. One likely candidate is the volume change associated with the conversion of alumina to a different phase at high temperature. To calculate D under the circumstances examined here, we envision that the coating diffuses into and may react with the top layer of alumina to form a new phase while the sample is at elevated temperature. The strain mismatch between the converted and unconverted regions can be expressed in terms of unit cell characteristic dimensions normalized by the proper number of alumina formula units. For pure polycrystalline Al₂O₃, the characteristic (isotropic) dimension, l , is given in terms of the mass density, ρ , as:

$$l = \left(\frac{MW}{\rho N_A n} \right)^{1/3} \quad (4)$$

where MW is the molecular weight, N_A is Avogadro's number, and n is the number of Al₂O₃ formulas in the unit cell. For Al₂O₃, l_{al} is thus 0.35 nm. The characteristic dimensions for other phases of interest are 0.40 nm for spinel, 0.37 for the CA₆ composition, and 0.42 for mullite. The formation of any of the new phases will thus lead to positive curvature, which is consistent with the direction of curvature obtained with all of the coatings. Ultimately, however, it is the degree of conversion, f , coupled with the lattice parameter difference that governs the magnitude of the strain mismatch arising from new i th-phase formation as:

$$D = f \frac{l_i - l_{al}}{l_{al}} = f\gamma \quad (5)$$

Equation (5) satisfies the limiting cases that for no

Table 1. Values of λ , D , and regression coefficients obtained by nonlinear regression for alumina substrates of different thickness coated with either MgO or CaO and heated to 1600 °C for 4 h

Coating	λ (–)	D (–)	R^2 (–)
MgO	4.4	0.072	0.87
CaO	1.0	0.21	0.89

Table 2. Possible phases present in the h_1 and h_2 regions along with the degree of conversion, (f_i), and the associated predicted strain mismatch for alumina substrates coated with MgO or CaO

Coating	Phases in the h_1 region (f_1)	Phases in the h_2 region (f_2)	Strain mismatch
MgO	0.67 MgAl ₂ O ₄ +0.33 Al ₂ O ₃ (0.65)	Al ₂ O ₃ (0)	0.096
MgO	MgAl ₂ O ₄ (1)	Al ₂ O ₃ (0)	0.143
CaO	CA ₆ (1)	Al ₂ O ₃ (0)	0.054

conversion, no strain mismatch occurs and for complete conversion, D is related to the lattice parameter difference between the original and new phase.

To obtain an estimate of f , we can proceed as follows. For CaO coatings on Al₂O₃, the plateau composition seen in Fig. 6 of CaO/Al₂O₃ $\approx$ 0.17 suggests that we are near the stoichiometric composition CA₆. Thus, for this composition, $f = 1$ and the corresponding strain mismatch is $D = 0.054$ (see Table 2). This value is about one quarter of the strain mismatch of 0.21 obtained by regression analysis.

For MgO coatings on Al₂O₃, the degree of conversion can be estimated to have either a value of $f = 1$, which, based on the plateau composition of MgO/Al₂O₃ $\approx$ 0.65, corresponds to an MgO-deficient spinel [7], or $f \approx 0.67$, which corresponds to a two-phase mixture of 0.67 spinel and 0.33 alumina. For these two cases (see Table 2), the strain mismatch D from the phase change alone ranges from 0.096-0.143, which is 20-50% higher than the value of $D = 0.072$ obtained by regression analysis.

Thus, we see that strain mismatch arising from the formation of new phase, while able to account for the direction of deformation, cannot account solely for the magnitude of the deformation. A second mechanism that can contribute to strain mismatch is differential shrinkage between the top and bottom layers of the substrate. The strain mismatch when both mechanisms are operative is then given as the difference between the top and bottom beam lengths, L_1 and L_2 , respectively, as [6]:

$$D = \frac{L_1 - L_2}{L_{10}} = \gamma_1 f_1 (1 - \varepsilon_v)^{1/3} + (s_2 - s_1) [1 - (1 - \varepsilon_v)^{1/3}] \quad (6)$$

where ε_v is the volume fraction of porosity and s_i denotes the fraction of void space of the i th layer that sinters fully. In Eq. (6), the first term on the right hand side describes strain mismatch from the reaction to the new phase whereas the second term describes strain mismatch from differential shrinkage between the two layers. The overall strain mismatch can thus lead to zero, positive, or negative curvature, depending on the relative values of the strain mismatch arising from new phase formation and from differential sintering.

As indicated by the microstructures in Figs. 7, differences in porosity between the top and bottom layers of the substrates are evident for MgO-coated substrates. More porosity is evident in the h_2 layer as compared to the h_1 layer, and, consequently, differential sintering will counteract, to some extent, the positive curvature arising from the phase change with a resultant lower overall curvature. This is qualitatively consistent with the results in Tables 1 and 2.

For CaO-coated substrates, the microstructures in Figs. 8 are more difficult to interpret, but the presence of the platy CA₆ phase in the h_1 layer suggests that it may have more porosity than the h_2 layer. If this is indeed the case, then differential sintering would exacerbate the positive curvature arising from the phase change; this is qualitatively consistent with the results in Tables 1 and 2.

In summary, then, the occurrence of a phase change accompanying the diffusion and reaction of the MgO and CaO coatings with the substrate accounts for the direction of the bilayer bending; differential sintering then further influences the magnitude of the curvature. For the SiO₂ coatings, a phase change may again account for the direction of bending. For these substrates, however, for which a trilayer model may be more appropriate, the overall mechanism is less clear. We note, however, that Si is found throughout the thickness of the substrate, and that very little porosity is evident in any of the layers. For this system, the presence of a liquid phase may have a stronger influence on the mechanics of bending and on the evolution of the microstructure, as compared to the magnesia and calcia systems.

Conclusions

A method has been developed to induce strain into alumina substrates coated with MgO, CaO, or SiO₂ at high temperature without applying external pressure. The amount of curvature depends strongly on a number of processing variables such as coating amount and type, substrate density and thickness, and hold temperature and time. For all three coatings, the direction of bending is consistent with the formation of a new phase which has a higher specific volume than the volume of the underlying alumina phase. In addition, differential sintering or porosity differences between the layers also influences the observed amount of curvature. The curvature dependence on the thickness of the two regions of the bilayer substrates can be explained by a viscoelastic mechanics model, with total mismatch strains of 7-20%.

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