

Reaction-bonding behavior of mullite ceramics with Y_2O_3 addition

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Abstract

Mullite ceramics were fabricated by a reaction-bonding technique from powder mixtures of Al_2O_3 and Si, with an Y_2O_3 addition. The mullitization and densification behavior was investigated as a function of Y_2O_3 content, heating rate, processing temperature and holding time as well as mullite seeds. It has been shown that mullite formation occurs by nucleation and growth within an aluminosilicate glass, but lattice and grain-boundary diffusion becomes important at the later stage of mullite growth. The addition of Y_2O_3 can decrease the glass viscosity and thus enhance the mullitization reaction, while the incorporation of mullite seeds may reduce the grain size and consequently allow pore elimination under conditions of shorter-range diffusion. After heating at $1400^\circ C$ for 5 h or $1450^\circ C$ for 2 h, an almost fully dense state was achieved for 15 mol% Y_2O_3 -doped and 5 mol% mullite-seeded specimens. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure-final; Mullite; Reaction bonding; Seeding

1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) has become a promising candidate for high-temperature structural applications in an oxidizing atmosphere due to its unique combination of advantageous properties such as low thermal expansion, high creep resistance, superior thermal stability, and excellent oxidation resistance.^{1–3} It has been shown that high-density mullite ceramics can be manufactured from powder mixtures of $Al_2O_3 + Al + SiC$ or $Al_2O_3 + Si$ via a reaction-bonding route at moderate temperatures ($1550^\circ C$).^{4–6} Recently, Mechnich et al.⁷ have demonstrated an accelerated reaction-bonding process by the addition of Y_2O_3 to the $Al_2O_3 + Si$ powder. However, the fundamental understanding of the process is currently limited. In this work, the effects of Y_2O_3 content, heating rate, processing temperature and holding time as well as mullite seeds on mullitization reaction and densification behavior are investigated and discussed.

2. Experimental procedure

Three commercial powders of $\alpha-Al_2O_3$ (>99.95%, Martoxid CS-400/M, Martinswerk GmbH, Bergheim, Germany), Si (99.5%, H. C. Starck, Goslar, Germany) and Y_2O_3 (>99.9%, HCST 4469, H. C. Starck, Berlin, Germany), which had a specific surface area of 10, 3.6 and $16 \text{ m}^2/\text{g}$, were used as the starting materials. The molar ratio of Al_2O_3 , Si and Y_2O_3 was taken as $3(100-x) : 2(100-x) : x$, with values of $x=5, 10$ and 15 . Prior to mixing, the as-received Si powder was ball milled in ethanol with Si_3N_4 balls at 300 rpm for 10 h to reduce the particle size. Cylindrical specimens of 15 mm in diameter and ~ 2 mm in thickness were prepared by die-pressing at a 100-MPa pressure. Reaction bonding was carried out in air using a one-step heating cycle in a box furnace at temperatures in the range of $1350\text{--}1450^\circ C$. Three different heating rates of 2, 5 and $10^\circ C/\text{min}$ were selected to determine the effects of heating rate on the reaction-bonding behavior. Bulk density and open porosity were measured by a water-immersion method. Phase analyses were performed by X-ray diffraction (XRD) using a computer-controlled diffractometer (D-5000, Siemens, Karlsruhe, Germany) with CuK_α radiation. Microstructures were observed on polished surfaces by scanning electron microscopy (SEM).

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3. Results and discussion

Generally, the oxidation of Si is very slow due to the formation of a protective SiO_2 layer on the surface. In order to achieve a complete Si oxidation in the reaction-bonding process, it was suggested that a low heating rate of $\leq 1^\circ\text{C}/\text{min}$ should be used.⁶ In the present work, however, the heating rate was observed to exhibit no significant effect on the oxidation reaction of Si to SiO_2 , as evidenced by the XRD patterns in Fig. 1. After heating at 1400°C for 2 h, no Si was detected in the specimens, regardless of the fact that the heating rate was up to $10^\circ\text{C}/\text{min}$. This should be attributed to the addition of Y_2O_3 , which may react with Al_2O_3 and SiO_2 to form a eutectic Y–Al–Si–O glassy phase at temperatures $\leq 1400^\circ\text{C}$.⁸ Since this low-viscosity Y–Al–Si–O glass may significantly enhance the diffusion of oxygen,⁷ the unoxidized Si during fast heating can be completely oxidized at the early stage of mullitization. Therefore, the heating rate becomes a less critical parameter for Si oxidation in this work.

Fig. 2 demonstrates the effect of heating rate on the density and porosity of 5 mol% Y_2O_3 -doped reaction-bonded mullite (RBM) ceramics which were heated at 1400°C for 2 h. Interestingly, the density increases and the porosity decreases as the heating rate increases. This is thought to be associated with the crystallization of oxidation-derived SiO_2 phase to cristobalite during heating. At a slow heating rate, the SiO_2 phase has more opportunity to crystallize. This may cause a decreased amount and/or an increased viscosity of the Y–Al–Si–O glass. As a consequence, densification through viscous-phase deformation would be limited, giving rise to a relatively low density. In light of this result, a high heating rate of $10^\circ\text{C}/\text{min}$ was used for further experiments.

It has been reported that the formation of mullite in the diphasic mixtures of $\alpha\text{-Al}_2\text{O}_3$ and SiO_2 occurs by

nucleation and growth within an amorphous aluminosilicate phase.^{9,10} Based on this mechanism, the rate of mullite formation is dependent on the rate of alumina dissolution into the siliceous glass. Considering the fact that the glass with a low viscosity favors the dissolution of alumina and that the addition of yttria may effectively decrease the viscosity of the siliceous glass,¹¹ a high degree of mullitization is expected to be obtained by the incorporation of more yttria. As shown in Fig. 1, 5 mol% Y_2O_3 -doped specimens exhibit a noticeable amount of cristobalite and α -alumina, indicating that the mullitization reaction is not complete. In contrast, mullitization is essentially complete in 15 mol% Y_2O_3 -doped specimen, as indicated in the XRD pattern of Fig. 3 by the elimination of the cristobalite (101) peak at $2\theta = 21.9^\circ$ and the decrease in the intensity of the α -alumina peaks. The presence of excess alumina in the specimens is because some SiO_2 was consumed due to the formation of yttrium silicate ($\text{Y}_2\text{Si}_2\text{O}_7$). By adjusting the Al_2O_3 : Si ratio in the initial powder composition, a RBM ceramic with less or even no residual alumina should be attainable. This issue remains under investigation.

Fig. 4 shows the dependence of bulk density and open porosity on Y_2O_3 additions for the RBM ceramics which were heated at 1400°C for 2 h with a heating rate

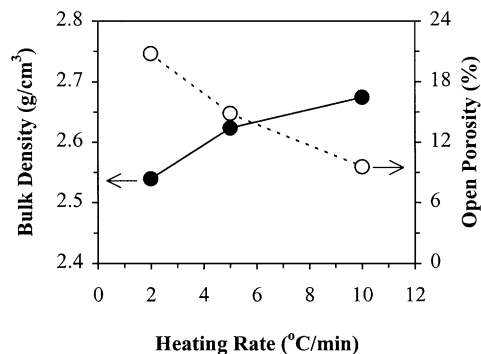


Fig. 2. Bulk density and open porosity as a function of heating rate for 5 mol% Y_2O_3 -doped RBM ceramics which were heated at 1400°C for 2 h.

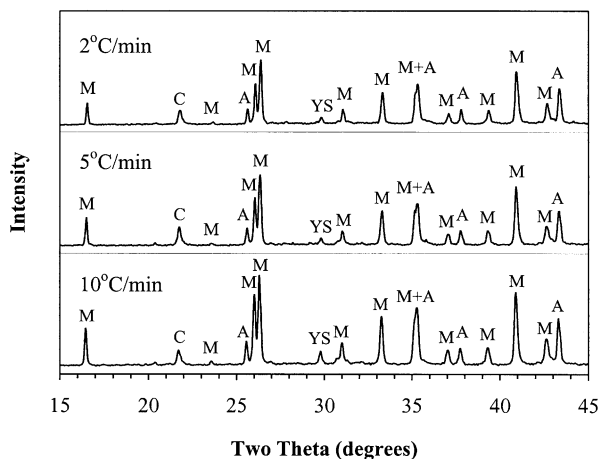


Fig. 1. XRD patterns of 5 mol% Y_2O_3 -doped specimens after heating at 1400°C for 2 h with three different heating rates (A is α -alumina, C is cristobalite, M is mullite, and YS is yttrium silicate).

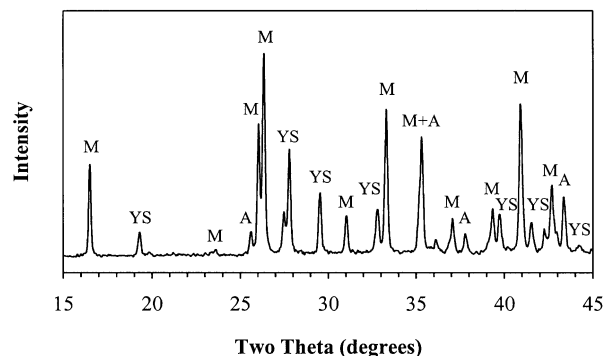


Fig. 3. XRD pattern of a 15 mol% Y_2O_3 -doped specimen after heating at 1400°C for 2 h with a heating rate of $10^\circ\text{C}/\text{min}$ (A is α -alumina, M is mullite, and YS is yttrium silicate).

of 10°C/min. As expected, the density increases and the porosity decreases with increasing Y_2O_3 content. However, a full densification has not been achieved even at an Y_2O_3 content of 15 mol%. This can be interpreted in terms of the mullite formation mechanism. As mentioned above, mullite forms by a nucleation and growth mechanism in an aluminosilicate glass. Specifically, mullite formation follows four distinct reaction steps:¹² (1) oxidation of Si to amorphous SiO_2 , (2) dissolution of alumina and yttria in the silica phase to form a Y–Al–Si–O glass, (3) nucleation of mullite within the alumina-saturated silicate glass, and (4) growth of mullite in the glass via continuous alumina dissolution. Since the nucleation of mullite takes place only at a limited number of sites,^{9,10} each grain may grow to a relatively large size until it encounters other growing grains, leaving some voids at the multigrain junctions. Such voids can be filled with the yttrious silicate glass. As the amount of the yttrious glass correlates directly to the addition of yttria, the residual porosity decreases as the yttria content increases. With 15 mol% yttria addition, the RBM specimens show an open porosity of ~4%. This indicates that a further increase in the yttria content is required to completely fill the void space with the yttrious glass. However, excessive yttria addition may lead to a decreased fraction of mullite in the final products. In addition, a higher densification degree was not observed for 15 mol% Y_2O_3 -doped RBM specimens by using a finer Si powder. Therefore, another way is required to achieve high densities.

Fig. 5 shows a typical SEM micrograph of 15 mol% Y_2O_3 -doped RBM ceramics. In this micrograph, the white, gray and light-gray phases correspond, on the basis of the energy-dispersive spectroscopy and the XRD pattern, to $Y_2Si_2O_7$, mullite and alumina, respectively. As can be seen, there is a notable amount of small rounded alumina particles in the mullite grains. This provides physical evidence for the proposed mechanism. Also, the elongated appearance of mullite grains is consistent with the growth of mullite in an amorphous phase, because the presence of a glassy

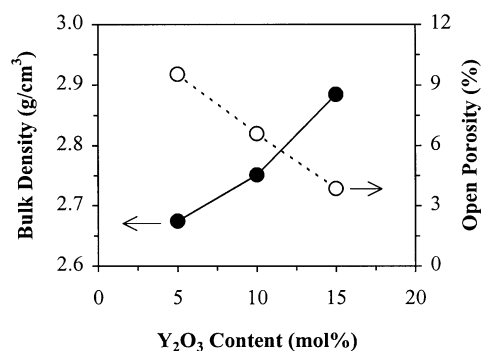


Fig. 4. Bulk density and open porosity versus Y_2O_3 content for the RBM ceramics, which were heated at 1400°C for 2 h with a heating rate of 10°C/min.

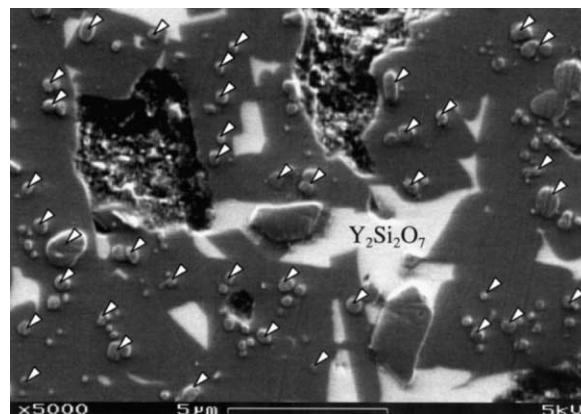


Fig. 5. SEM micrograph of a polished surface for a 15 mol% Y_2O_3 -doped RBM specimen after heating at 1400°C for 2 h. Some of the unreacted α -alumina particles are indicated by arrows.

phase is one of the necessary conditions for the growth of anisotropic mullite grains, especially in the Al-rich composition.¹³ However, such a glass was not observed in the final products. This can be explained as follows: the concentration of the yttrious silicate glass increases with the growth of mullite grains due to the consumption of the siliceous phase. When the yttrious glass reaches the $Y_2Si_2O_7$ composition, crystallization occurs, leading to the disappearance of the yttrious silicate glass and the formation of the crystalline $Y_2Si_2O_7$ phase. As shown in Fig. 5, the $Y_2Si_2O_7$ phase is located mostly at the multigrain junctions and partly at the grain boundaries, but never present within the mullite grains. This is not surprising, because the yttrious silicate glass can be saturated only at the late stage of mullite growth.

On the other hand, it can be observed in Fig. 5 that some large pores are formed at the multigrain junctions. The elimination of such pores requires mass transport through the lattice dislocations and/or the grain boundaries.^{14,15} Owing to the low lattice and grain-boundary diffusion coefficients for mullite,³ the pores are difficult to remove, especially in the case of a large mullite grain size. This may account for the results of the density measurements in Fig. 6 that the porosity in 15 mol% Y_2O_3 -doped RBM specimens decreases only from ~4 to ~2% with an increase in the holding time from 2 to 10 h at 1400°C. As indicated earlier, the development of large mullite grains in the RBM process is due to a relatively low number of mullite growth sites. Since crystalline mullite seeds are highly effective as mullite growth sites,^{9,10,16,17} the mullite grain size is expected to be reduced by the incorporation of fine mullite particles into the initial powder mixtures. In the present work, a commercially available aluminosilicate precursor (Siral II, Condea Chemie, Hamburg, Germany) was used as the mullite seeds after crystallization at 1400°C for 5 h. It is evident from the SEM micrographs in Figs. 5 and 7(a) that the seeded specimen has a considerably smaller mullite grain size than the

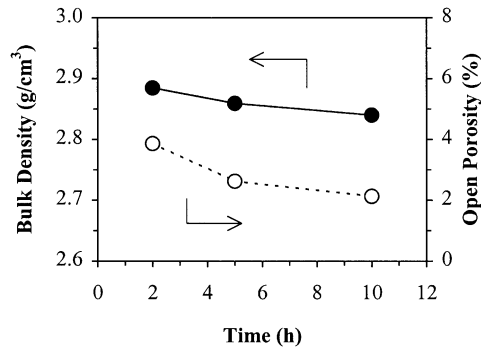


Fig. 6. Bulk density and open porosity as a function of holding time at 1400°C for 15 mol% Y_2O_3 -doped RBM ceramics.

unseeded specimen. However, some faceted pores are still present at the multigrain junctions, giving a low density of only 2.85 g/cm^3 . For this reason, an increase in the holding time was applied at a temperature of 1400°C. As shown in Fig. 8, the density increases from 2.85 to $\sim 3.18 \text{ g/cm}^3$ and the corresponding porosity decreases from ~ 12 to $\sim 1\%$ as the holding time increases from 2 to 5 h. This is quite different from the results of the unseeded specimens in Fig. 6. As stated above, the elimination of the faceted intergranular pores requires mass transport by lattice diffusion and/or grain-boundary diffusion. In the seeded specimens, the

diffusion distances are relatively short due to a smaller mullite grain size. This allows the pores to be removed at longer times. Fig. 7(b) shows the microstructure of a seeded specimen after heating at 1400°C for 5 h. Evidently, the specimen is almost fully densified. An additional increase in the holding time from 5 to 10 h does not significantly affect the microstructure. As shown in Fig. 7(c), the grains retain an elongated morphology and some small pores can be observed occasionally at the intergranular positions.

Fig. 9 shows the XRD pattern of a 15 mol% Y_2O_3 -doped and 5 mol% mullite-seeded RBM specimen after heating at 1400°C for 2 h. As shown, the specimen contains mullite, alumina and $Y_2Si_2O_7$. When the holding time was extended to 5 h or even to 10 h, no significant changes were observed in the XRD patterns, except for a small increase in the intensity of the $Y_2Si_2O_7$ peaks. This indicates that the mullitization reaction is almost complete in the specimen after a 2 h holding at 1400°C. With a further increase in the holding time, the classical densification mechanism, i.e. lattice and grain-boundary diffusion, would be operative. This is consistent with the microstructural observations in Fig. 7.

Fig. 10 shows the bulk density and open porosity of the seeded and unseeded specimens after heating at

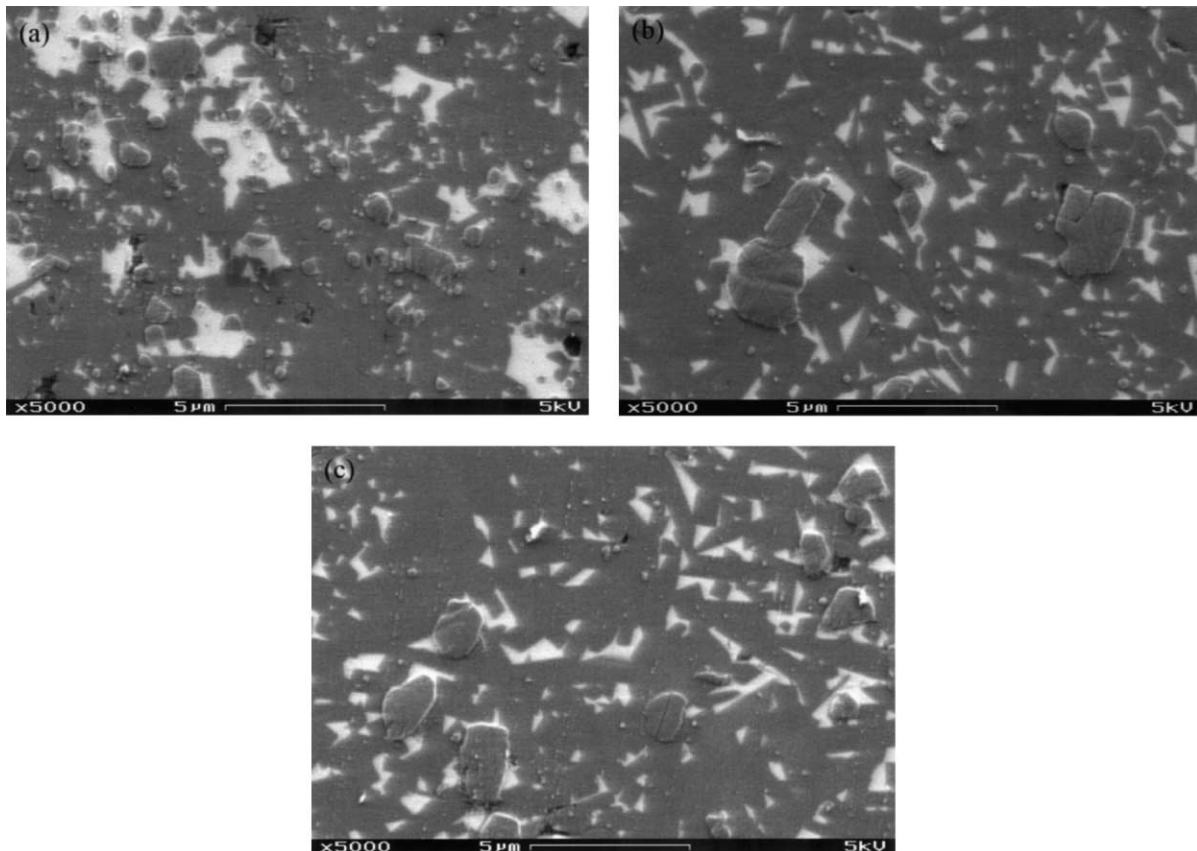


Fig. 7. Microstructures of 15 mol% Y_2O_3 -doped and 5 mol% mullite-seeded RBM ceramics after heating at 1400°C for (a) 2 h, (b) 5 h and (c) 10 h.

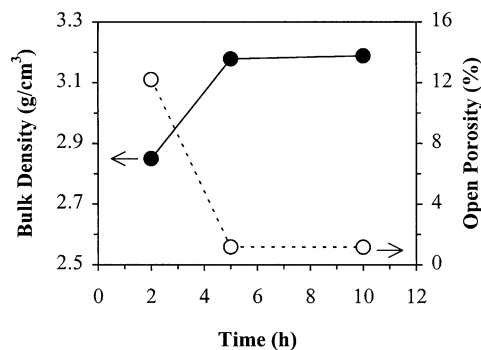


Fig. 8. Bulk density and open porosity as a function of holding time at 1400°C for 15 mol% Y_2O_3 -doped and 5 mol% mullite-seeded RBM ceramics.

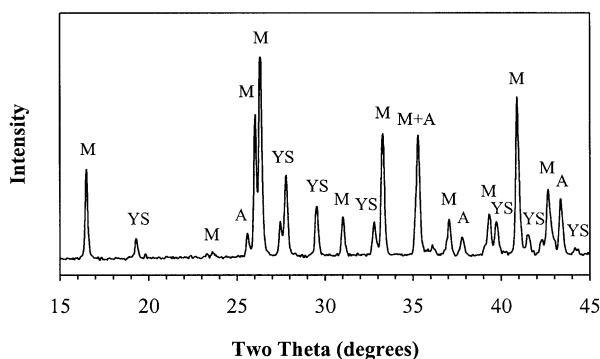


Fig. 9. XRD pattern of a 15 mol% Y_2O_3 -doped and 5 mol% mullite-seeded RBM specimen after heating at 1400°C for 2 h (A is α -alumina, M is mullite, and YS is yttrium silicate).

three different temperatures of 1350, 1400 and 1450°C for 2 h. These results are consistent with the argument that densification occurs by lattice and grain-boundary diffusion at the later stages of the RBM process. Since the lattice and grain-boundary diffusion becomes faster at higher temperatures, the density increases and the porosity decreases with the processing temperature. In the seeded specimens, smaller mullite grain sizes allow shorter-range diffusion and consequently more rapid densification. As shown in Fig. 10, a high density of ~ 3.18 g/cm³ and a low porosity of $< 1\%$ is obtained for the seeded specimen at 1450°C. In contrast, only a little improvement in densification was observed for the unseeded specimens. However, it is noteworthy that the densification degree is lower for the seeded specimens in comparison with the unseeded specimens at 1350 and 1400°C. This is probably due to a very low sintering activity of mullite particles, especially at lower temperatures. In addition, it is interesting that the unseeded specimen exhibits a slight decrease in bulk density at 1450°C. This should be attributed to a more complete mullitization reaction between alumina and silica at higher temperatures, because such a reaction may lead to a $\sim 3\%$ volume expansion.⁹ Also, the slight decrease of bulk density with holding time in Fig. 6 is a result of additional mullite formation.

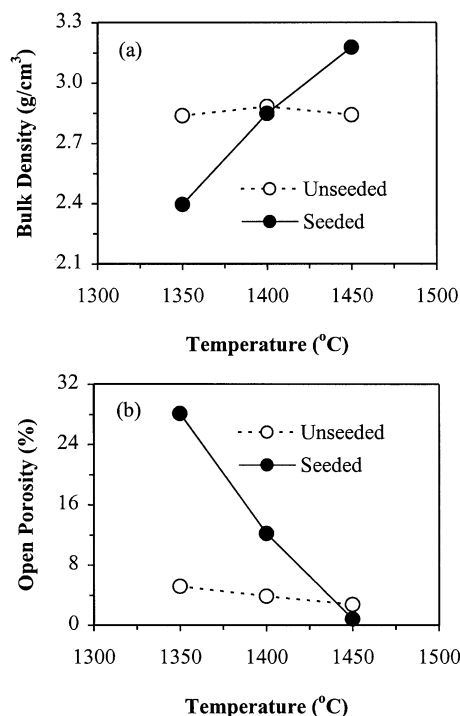


Fig. 10. Variation of (a) bulk density and (b) open porosity with processing temperature for seeded and unseeded specimens.

4. Conclusions

A recently-developed RBM technology was employed to fabricate mullite ceramics at relatively low temperatures from the powder mixtures of Al_2O_3 and Si, with an Y_2O_3 addition. The effects of Y_2O_3 content, heating rate, processing temperature and holding time as well as mullite seeds on the mullitization and densification behavior were investigated. Owing to the formation of a low-viscosity Y–Al–Si–O glass in the process, Si oxidation and mullite formation were observed to be significantly enhanced. In addition, it has been shown that mullitization occurs via a nucleation and growth mechanism, but lattice and grain-boundary diffusion becomes important during the late stages of the mullitization reaction. This necessitates the incorporation of mullite seeds to obtain a smaller grain size and a higher densification degree. With 15 mol% Y_2O_3 and 5 mol% seeds, the specimens can reach an almost fully dense state after heating at 1400°C for 5 h or 1450°C for 2 h. Moreover, a good high-temperature behavior is expected due to the absence of glassy phases in the final products.

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