Reaction bonding of mullite (RBM) in presence of scandia Sc_2O_3

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Abstract

The presence of 3rd group transition metal oxides yttria and lanthana has a strong accelerating influence on the reaction bonding of mullite (RBM) from silicon and α-alumina, even at temperatures below 1350 °C. This is due to the formation of low-viscosity transient liquid phases enhancing Si-oxidation, alumina diffusion and mullite nucleation and growth. The presence of the 3rd group transition metal oxide scandia (Sc_2O_3) does not show a significant influence on the RBM process up to 1350 °C. Sc_2O_3 does not form low viscous Sc–Al–Si–O liquid phases which enhance reactivity. Instead, a direct formation of Sc-disilicate $Sc_2Si_2O_7$ is observed. At temperatures between 1350 and 1550 °C, a slightly enhanced mullite formation due to accelerated solid state diffusion, and the formation of a ternary Sc-rich aluminosilicate is evident.
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1. Introduction

The reaction bonding of mullite (RBM) is considered a promising technology for the near-net-shape processing of mullite ceramics and composites. Sintering-induced volume shrinkage is partially counterbalanced by oxidation-controlled volume expansion of non-oxide starting powders like SiC, Si and Al. After the oxide formation the constituents react to mullite. Wu and Claussen[1], Wu et al.[2] and Holz et al.[3] demonstrated methods for the fabrication of RBM–SiC and RBM–ZrO2 composites by employing Al metal, SiC, α-Al2O3 and ZrO2 as starting materials. The RBM process is also considered highly attractive for the processing of continuous fiber-reinforced ceramic matrix composites (CMCs). In this case, matrix cracking associated with sintering-induced shrinkage is prevented by oxidation-controlled expansion of non-oxide starting powders. However, the reaction of pure Al_2O_3 and SiO_2 to mullite requires high processing temperatures (>1500 °C) which are detrimental to polycrystalline fibers by causing significant grain growth resulting in loss of fiber strength. In order to solve this problem, a method to fabricate substantially glass-free RBM ceramics at significantly lower processing temperatures has been developed by Mechnich et al.[4,5] They showed that the addition of Y_2O_3 to the starting compositions, consisting of Si metal powders plus α-alumina and precursor-derived mullite seeds,

has a strong accelerating influence on RBM processing. The mechanism of the accelerated reaction bonding process is the formation of a low-viscosity transient Y–Al–Si–O liquid phase, providing enhanced diffusion of species and, as a consequence, accelerated Si metal oxidation and mullite formation. The essential feature of this RBM route is that after heat treatment at $T = 1300–1350$ °C, the coexisting liquid phase completely recrystallizes to Y-silicate Y_2SiO_7. The influence of Y_2O_3 on the phase formation in reaction sintered mullite (RSM), i.e. in mixtures of Al_2O_3 and SiO_2 was investigated by She et al.[6] and Kong et al.[7] They found basically the same beneficial influence of Y_2O_3-doping on the mullite formation kinetics as in case of the RBM systems. Kong et al.[7] also investigated the influence of La_2O_3 on the phase formation in RSM-systems and found a similar accelerated mullite formation. However, in this case, the observed La–Al–Si–O liquid phase does not have a transient character, i.e. the formation of a crystalline La-containing phase was not observed after processing. This means that La_2O_3-doping is not suitable for the fabrication of glass-free RBM ceramics. Little information has been given on the behavior of the other 3rd group transition metal oxide scandia (Sc_2O_3) in mullite systems so far. The present study was performed in order to evaluate the potential of Sc_2O_3-doping for processing of RBM ceramics.

2. Experimental procedure

Si metal powders (H.C. Starck Goslar, Germany, purity 99.5%) were pre-milled for 12 h in isopropyl alcohol with Si_3N_4

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milling balls. After drying and sieving of the milled powders, a Si surface area of about $40\,m^2/g$ was measured (Area-Meter, Strohlein, Germany). α-Al_2O_3 powders (Martoxid CS 400/M, Martinswerk Bergheim, Germany, purity >99.95%) and scandia powders (>99, 5%, Ventron, Karlsruhe) were used without pretreatment. Mullite precursor powders (Siral 28, Sasol, Hamburg, Germany), consisting of γ-alumina and amorphous silica were annealed at $1350\,^{\circ}C$ for 2 h and subsequently employed as mullite seeds having a surface area of $\approx25\,m^2/g$.

The composition of the reference RBM powder mixtures was calculated based on the stoichiometric composition $(3Al_2O_3 + 2Si)$ of which 5 wt.% was replaced by mullite seeds. This leads to a starting composition of 14.74 wt.% Si, 80.26 wt.% Al_2O_3 and 5.0 wt.% mullite seeds, respectively. The Sc-doped RBM powder mixtures were adjusted to a Sc-content of 2.1 mol% on the metals basis (see Mechnich et al.[4]) leading to a starting composition of 14.29 wt.% Si, 77.75 wt.% Al_2O_3, 4.85 wt.% mullite seeds and 3.1 wt.% Sc_2O_3, respectively. Taking into account that the as-received Si metal contains ≈0.5 wt.% impurities (mainly Fe and Al) and ≈1 wt.% oxygen, a slight Si deficiency with respect to stoichiometric mullite is assumed. The powder mixtures were homogenized for 2 h in a planetary ball mill with Si_3N_4 milling balls in isopropyl alcohol, dried and passed through a $250\,\mu m$ sieve. The powders were pressed into bars of $55\,mm \times 5\,mm \times 4\,mm$, using an applied pressure of 50 MPa. The as-fabricated bars were vacuum sealed in latex tubes and cold isostatically pressed at 200 MPa.

The degree of processing-related Si-oxidation was determined via weight changes of specimens during heat treatments using thermogravimetric analyses. Experiments were performed with a Netzsch STA 409 thermobalance in air up $1350\,^{\circ}C$. To monitor the temperature-dependent reaction processes, samples were heated up with a heating rate of 5 K/min in air in a resistor-heated chamber furnace (Ceram-Aix, Aachen, Germany) to test temperatures between 1250 and $1600\,^{\circ}C$, and then quenched in air. Phase analyses were carried out by X-ray powder diffractometry (XRD) (D5000, Siemens, Karlsruhe, Germany) in step scan mode and Cu Kα radiation (wavelength: 1.5418 Å). Microstructural analyses were carried out using a LEO DSM scanning electron microscope with field emission cathode and energy dispersive X-ray elemental analysis.

3. Results

3.1. Oxidation behavior and phase formation at 1350 °C

The first set of experiments was performed in accordance to the work by Mechnich et al.[4] in order to evaluate the potential of Sc-doping for rapid processing of RBM at a target temperature of $1350\,^{\circ}C$. The temperature- and time-dependent oxidation of Si is directly correlated to the thermogravimetric curves of undoped and Sc-doped RBM samples (Fig. 1). The undoped (dotted line) and Sc_2O_3-doped (solid line) RBM samples display the typical sigmoidal shape of diffusion-controlled Si-oxidation.[8] At $1350\,^{\circ}C$ a weight gain of about 13% is achieved in both samples which further increases slowly within the 5 h holding time. Both samples display almost identical oxidation behavior during the
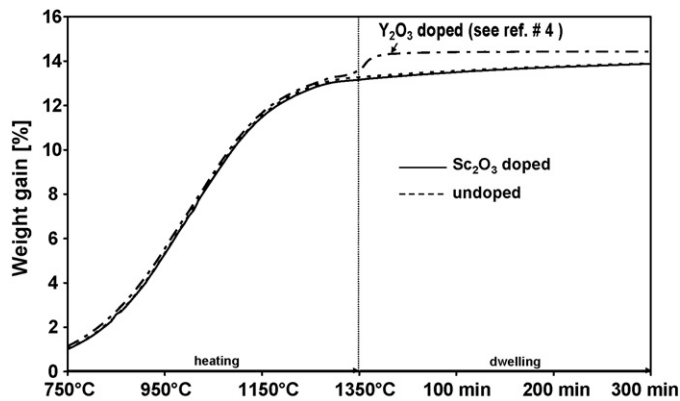

Fig. 1. Si-oxidation induced weight changes of undoped (dashed line) and Sc_2O_3-doped (solid line) RBM samples. Specimens were initially heated up at a rate of 2 K/min to $1350\,^{\circ}C$ and then held at this temperature for 5 h. Undoped and Sc_2O_3-doped samples display an almost identical oxidation behavior. For comparison a Y_2O_3-doped RBM-sample is also displayed.[4] Oxidation of the Y_2O_3-doped sample is discontinuous, with a strong increase at $1300\,^{\circ}C$.

following dwelling time at $1350\,^{\circ}C$, reaching a weight gain of about 14% after 5 h at $1350\,^{\circ}C$. However, the slope of the weight gain curve indicates that even after 5 h at $1350\,^{\circ}C$ a significant fraction of the Si is still present. From this result, it is obvious that Sc-doping has essentially no accelerating influence on the Si-oxidation. For comparison, the weight gain curve of an analogous, Y_2O_3-doped sample is also plotted in Fig. 1. (data from Mechnich et al.[4]) This sample exhibits a similar behavior up to about $1330\,^{\circ}C$, however, followed by a sharply accelerated oxidation around $1350\,^{\circ}C$. The final weight gain of $\approx14.5\%$ is reached must faster, i.e. after approximately 120 min at $1350\,^{\circ}C$.

The temperature- and time-dependent phase development of undoped reference RBM compared to Sc-doped RBM was determined by XRD and SEM. The XRD results are given in Fig. 2 for samples heated at $1350\,^{\circ}C$ for 5 h. The presence of oxidation-derived, cristobalite (SiO_2) is observed in both sam-
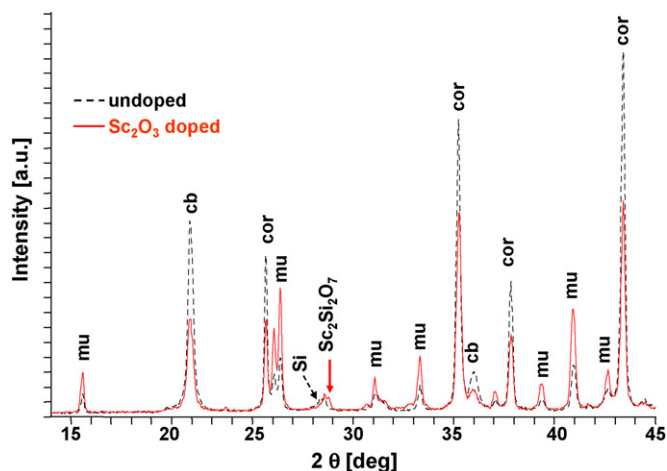

Fig. 2. X-ray powder diffraction profile of undoped (dashed line) and Sc_2O_3-doped (solid line) RBM samples after 5 h annealing at $1350\,^{\circ}C$. Undoped RBM shows a very low mullite content and residual Si. Although Sc_2O_3-doped RBM samples show formation of mullite (mu) at the expense of α-alumina (cor) and cristobalite (cb), reaction is still sluggish. After annealing, Sc_2O_3 is present as Sc-disilicate $Sc_2Si_2O_7$.
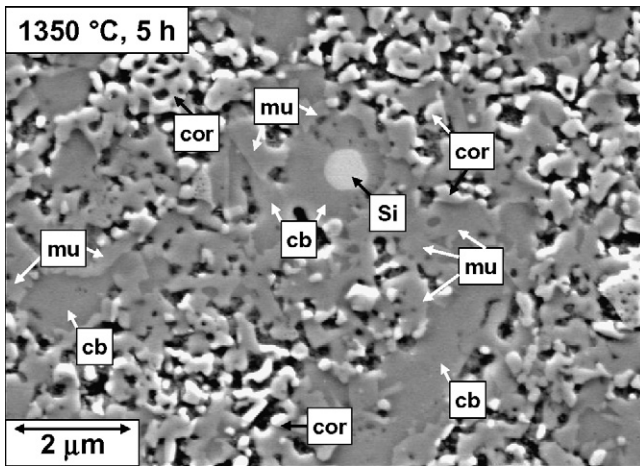
Fig. 3. Microstructure of undoped RBM samples after 5 h annealing at 1350 °C. SEM-image of polished cross-section shows residual Si enveloped by cristobalite (cb). Prismatic mullite (mu) grows at the interface between cristobalite (cb) and fine α-alumina (cor).

ples. However, the Sc-doped RBM sample contains a significant lower amount of cristobalite, along with a significant lower amount of α-alumina and significantly higher mullite content. Undoped RBM sample still contain significant amount of Si as indicated by a diffraction peak at a 2θ value of $\approx28°$. In addition to some residual Si, Sc-doped samples show a small diffraction peak at $\approx29°$ 2θ which is related to the presence of the Sc-silicate $Sc_2Si_2O_7$ (thortveitite). The SEM analyses of polished cross-sections confirm the results obtained by XRD: the microstructure of the undoped RBM sample (Fig. 3) shows residual, equiaxed Si grains (light gray) enveloped by SiO_2 (cristobalite) along with small alumina grains. Prismatic mullite crystals are typically located at the interface of cristobalite and alumina. The Sc-doped RBM sample exhibits a similar microstructure (Fig. 4), however, with some additional Sc-disilicate $Sc_2Si_2O_7$. Although the density of the Sc-doped sample seems somewhat higher than
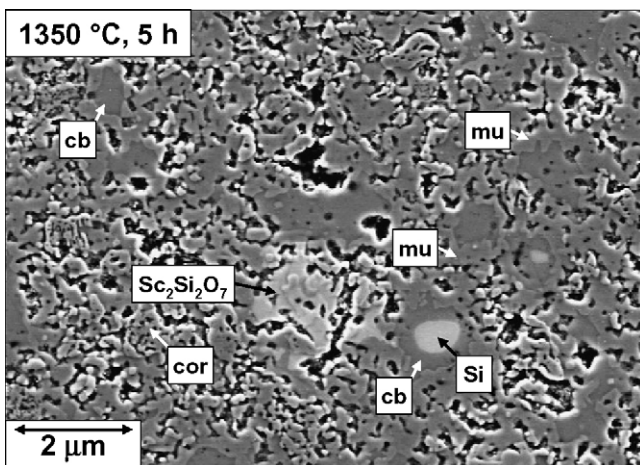

Fig. 4. Microstructure of Sc_2O_3-doped RBM samples after 5 h annealing at 1350 °C. SEM-image of polished cross-section shows residual Si enveloped by cristobalite (cb). Prismatic mullite (mu) grows at the interface between cristobalite and fine α-alumina (cor). Sc_2O_3 has reacted to light gray contrasted $Sc_2Si_2O_7$.

the undoped material, there is no evidence for the formation of a liquid phase.

3.2. Phase formation between 1250 and 1550 °C

Up to 1350 °C the Sc_2O_3-doping has no accelerative influence on Si-oxidation and limited influence on mullite crystallization of RBM samples, if compared to Y-doped RBM-systems. A second set of experiments was performed in order to evaluate the temperature-dependent phase development at higher temperatures. For this purpose, undoped RBM and Sc_2O_3-doped RBM samples were annealed together to test temperatures ranging from 1250 to 1550 °C with heating rates of 5 K/min and quenched in air. The phase contents of these samples were determined by XRD and the microstructures of selected samples were analyzed by SEM. The mullite content was calculated using the integral peak intensity ratio of mullite (mu) XRD reflections (1 2 0) and (2 1 0) and α-alumina (cor) XRD reflection (1 1 3) according to mu (wt.%) = $(I_{(mu120)} + I_{(mu210)})/(I_{(mu120)} + I_{(mu210)} + I_{(cor113)})$ which is quite accurate measure for the mullite content of RBM samples.[9] Fig. 5 gives the temperature-dependent mullite content of undoped (dotted line) and Sc_2O_3-doped (solid line) RBM samples. No difference between both samples can be detected at temperatures up to 1300 °C. At 1350 °C, the mullite content of the Sc-doped sample is around 5% higher than in the undoped sample. The difference then increases to about 18% at 1400 °C and finally goes up to around 25% between 1450 and 1550 °C. At 1550 °C the calculated mullite content of the Sc_2O_3-doped RBM is almost 100% whereas the undoped RBM only reaches a value of about 75%. Microstructural analyses were carried out using polished cross-sections of samples quenched at 1350 and 1500 °C, respectively. At 1350 °C the undoped RBM sample essentially consists of fine grained alumina partially infiltrated with silica (cristobalite) and some residual Si surrounded by cristobalite (Fig. 6a). At 1500 °C, a significant densification occurred, along with a pronounced silica infiltration and subsequent conversion to
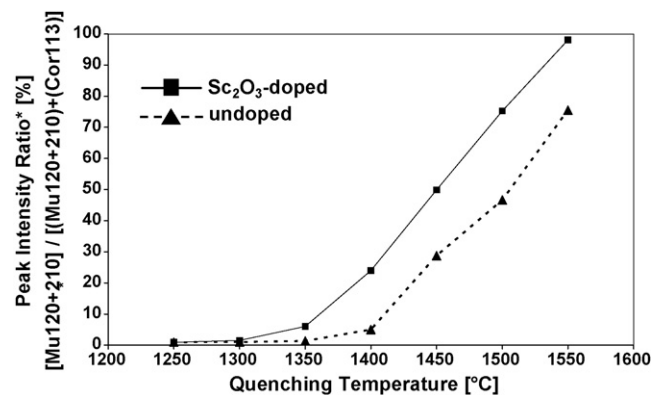

Fig. 5. Mullite content of RBM samples after quenching, determined by X-ray powder diffraction and peak intensity analyses. Undoped RBM (dashed line) shows negligible mullitization at 1350 °C followed by an increase up to 75% at 1550 °C. Sc_2O_3-doped RBM samples (solid line) show a significant mullitization at 1350 °C and nearly complete reaction at 1550 °C.
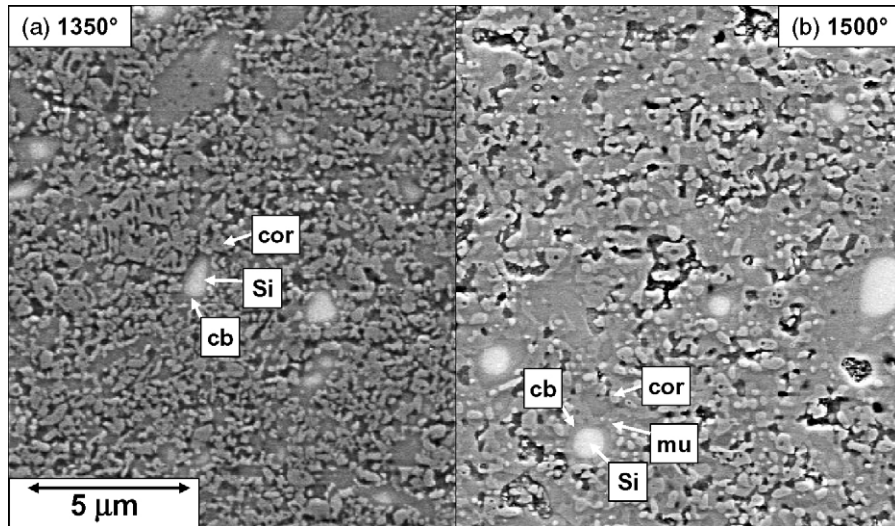
Fig. 6. Microstructure of rapidly quenched, undoped RBM samples (polished cross-section). At 1350 °C ((a) left-handed side) samples consist of residual Si enveloped by cristobalite (cb) along with fine-grained α-alumina (cor). At 1500 °C ((b) right-handed side) samples show globular Si enveloped by cristobalite (cb) along with fine-grained α-alumina (cor) and prismatic mullite (mu).

prismatic mullite. Even at 1500 °C, there are residual Si grains with nearly globular shape, which is caused by Si-melting above 1420 °C (Fig. 6b). The Sc_2O_3-doped sample exhibits a similar microstructure at 1350 °C with residual Si, fine grained α-alumina and cristobalite, in addition platelet-like grains of Sc_2O_3 are visible (Fig. 7a). At 1500 °C the microstructure of the Sc_2O_3-doped RBM changes: the alumina content is significantly lower at the expense of mullite. Nevertheless, residual globular Si grains can still be found (Fig. 7b). Regarding the platelet-like Sc_2O_3-grain, there seems to be no dramatic visible change in morphology that means a melting process obviously did not occur. However, this Sc_2O_3-grain evidently shows a kind of reaction zone as indicated by a different contrasted core and rim. A closer look reveals that both core and rim are polycrystalline (Fig. 8). EDX-analyses proved the fairly lighter

core to be (residual) Sc_2O_3. The EDX-analysis revealed that the rim contains Sc_2O_3, Al_2O_3 and SiO_2. In order to verify this finding, 10 individual grains with reaction rims were analyzed. The mean composition was found to be 21.65% Sc, 8.55% Al, 3.85% Si and 65.95% O. Calculating as oxide the approximate composition results in $10Sc_2O_3 \cdot 4Al_2O_3 \cdot 3SiO_2$. Taking into account the highly faceted character of the reaction rim and the low scattering of the chemical analysis, the formation of a crystalline Sc_2O_3-rich ternary phase can be assumed. However, inspection of the ICDD powder diffraction database did not lead to matching ternary phases. Set #42-0159 describes a phase having a composition of $Sc_4Al_6Si_3O_{21}$; Set #48-1614 describes a phase with a composition of $Sc_{0.8}Al_{1.9}Si_{0.3}O_{4.7}$. Both phases obviously do not have the chemical composition found in this study.
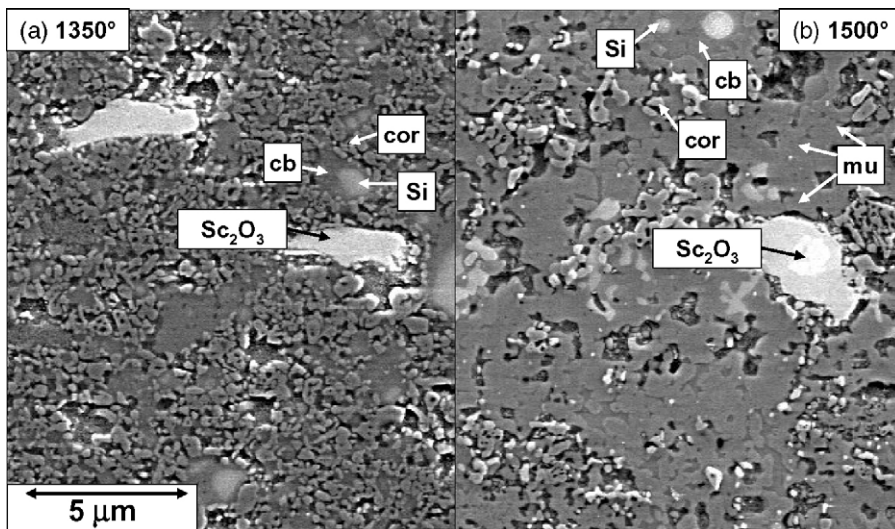

Fig. 7. Microstructure of rapidly quenched, Sc_2O_3-doped RBM samples (polished cross-section). At 1350 °C ((a) left-handed side) samples consist of tabular Sc_2O_3, residual Si enveloped by cristobalite (cb) along with fine-grained α-alumina (cor). At 1500 °C ((b) right-handed side) samples show some Si enveloped by cristobalite (cb) along with some fine-grained α-alumina (cor) and large areas of mullite (mu). The Sc_2O_3-grain shows a significant contrast with a bright core area.
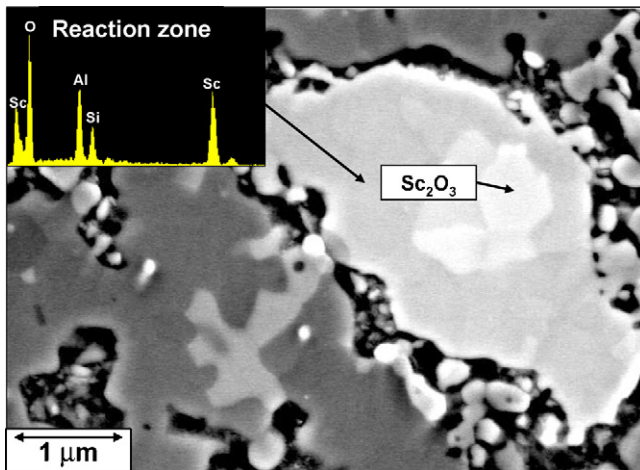
Fig. 8. Microstructure of Sc_2O_3-doped RBM samples rapidly quenched from 1500 °C. The close-up view confirms a reaction zone around the Sc_2O_3-grain. From EDX-analysis the core consists of pure Sc_2O_3 whereas he rim is a ternary Sc-aluminosilicate phase having an approximate composition of $10Sc_2O_3 \cdot 4Al_2O_3 \cdot 3SiO_2$.

4. Discussion

The results of previous studies[4,6,7] and the present work show that the 3rd group transition metal oxides scandia, yttria and lanthana (La_2O_3) behave quite differently if employed as oxide dopants for reaction based processing of mullite. In our case, RBM samples based on α-alumina and Si-metal were investigated. During heat treatment, oxidation-derived amorphous SiO_2 layers grow around the Si grains. They act as diffusion barriers for oxygen, and, therefore, increasingly slow down the oxidation velocity. Above 1200 °C, the non-crystalline SiO_2 layers begin to transform into cristobalite. Even at 1550 °C the reactivity of the almost chemically pure SiO_2 layers enveloping the Si-grains still is too low for sufficient dissolution and diffusion of Al_2O_3. As a consequence, the Al super saturation in the liquid required for mullite nucleation and growth cannot be achieved in short periods of time. In Y_2O_3- or La_2O_3-doped RBM the formation of low-viscous Y–Al–Si–O or La–Al–Si–O liquid phases above 1300 °C strongly accelerates oxidation of Si-metal and mullite formation. These newly formed liquid phases can easily penetrate into the matrix and interact with SiO_2-layers enveloping the Si grains. As a result, the SiO_2 layers which normally act as diffusion barriers for oxygen are partially removed. The low viscous melts also provide improved Al_2O_3-dissolution and diffusion as compared to pure SiO_2. Therefore, the super saturation of Al, the precondition for mullite nucleation and growth is achieved. Whereas the Y–Al–Si–O melts show a transient behavior, i.e. re-crystallize to Y-silicate after processing, the La–Al–Si–O melts remain as amorphous phases in the RBM ceramics. In the case of Sc_2O_3-doped RBM, low-viscous melts do not occur and Sc_2O_3 obviously directly crystallized to the Sc-disilicate $Sc_2Si_2O_7$ via a solid state reaction, as indicated by the similar grain shape of initial Sc_2O_3 and final $Sc_2Si_2O_7$. As a consequence, there is no evidence for any accelerated Si-oxidation up to 1350°. Even at 1550 °C, accelerated Si-oxidation was not observed, indicated by residual Si-grains enveloped by

SiO_2-layers. However, it should be noted that the mullite formation kinetics was significantly higher than that of undoped RBM. There might be two possible reasons for this: on the one hand, mullite formation could be triggered in the surroundings of Sc_2O_3-grains by a transient, highly viscous Sc–Al–Si–O liquid phase which does not penetrate the microstructure. On the other hand, an accelerating solid state diffusion mechanism could be responsible for enhanced mullite growth.

Interestingly, the formation of a coexisting crystalline, Sc-rich aluminosilicate was observed at $T > 1450$ °C instead of the silicate $Sc_2Si_2O_7$ observed at lower temperatures. The grain shape of this phase typically seems to follow those of the initial Sc_2O_3-grain. A conclusion would be that the formation occurred via solid state diffusion rather than co-melting and re-crystallization of either initial Sc_2O_3 or transient $Sc_2Si_2O_7$. Following this scenario, the enhanced mullite formation is also probably associated to an enhanced solid state diffusion. An interesting question is the true nature of the coexisting Sc-rich aluminosilicate phase. The microanalysis clearly indicated that this phase shows a constant chemical composition of about $10Sc_2O_3 \cdot 4Al_2O_3 \cdot 3SiO_2$. Up to this point, a phase of this composition was not described in the literature and standard material databases. It is suggested that it can also be synthesized via reaction sintering of oxides.

5. Summary and outlook

Unlike yttria (Y_2O_3) and lanthana (La_2O_3), scandia does not exhibit a significant accelerative influence on the reaction bonding of mullite using powder compacts of Si-metal and α-Al_2O_3 up to temperatures of 1350 °C. Sc_2O_3 does not form low viscous Sc–Al–Si–O liquid phases which enhance diffusion of species. Instead, a direct formation of Sc-disilicate $Sc_2Si_2O_7$ (thortveitite) is observed. At temperatures between 1350 and 1550 °C, an increasingly enhanced mullite formation due to accelerated solid state diffusion is evident. Additionally, the formation of a crystalline Sc-rich aluminosilicate having a chemical composition of about $10Sc_2O_3 \cdot 4Al_2O_3 \cdot 3SiO_2$ is observed at $T > 1450$ °C. At this point, the nature of this co-existing phase remains speculative. Experiments including synthesis of this phase and related chemical, structural and microstructural analysis are currently underway.

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