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Thermo-mechanical properties of mullite–zirconia composites derived from reaction sintering of zircon and sillimanite beach sand: Effect of CaO

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Abstract: Mullite–zirconia composites containing 20% zirconia (mass fraction) were prepared by reaction sintering route utilizing Indian coastal zircon flour and sillimanite beach sand. 4%−12% of CaO (mole fraction) with respect to zirconia was used as additive. The effect of additive on densification, microstructure as well as various mechanical and thermo-mechanical properties was studied. Incorporation of CaO reduced the densification temperature of the composites to 1550 °C compared to 1600 °C (for CaO free samples). CaO formed small amount of liquid phase (calcium aluminosilicate), which facilitated sintering. Average grain size of the composites decreased up to 4% CaO addition, afterwards grain size increased with further addition of CaO. Samples with 4% CaO exhibited ~225 MPa of flexural strength, ~6 $\mathrm{MPa\cdot m^{1/2}}$ of fracture toughness and significant improvement in thermal shock resistance. CaO stabilized the tetragonal zirconia phase and thus improved the mechanical properties.

Key words: reaction sintering; mullite−zirconia composites; flexural strength; refractory

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1 Introduction

Mullite−zirconia composites are the well-recognized refractory materials due to their superior thermo-mechanical properties and mainly used in glass industries in different areas of the glass melting tank [1−3]. Attempts were made to synthesize such composites using various starting materials [4−8] and different processes [9−14]. But, most of the researchers have utilized purer grade raw materials, which have inadequate availability.

In India, there are huge deposits of rare earth containing beach sand minerals, which generate enormous quantity of zircon and sillimanite beach sands during extraction of rare earth compounds as by products [15]. Reaction sintering of zircon and sillimanite sand may be a cost competitive route of the preparation of mullite−zirconia composites. Sillimanite sand decomposes into mullite and amorphous silica on heat treatment [16,17]. The presence of free silica has negative impact on the thermo-mechanical properties of developed materials. Product quality can be significantly improved by adding proper amount of alumina in the batch, so it can chemically react with released amorphous silica and form further mullite [18].

Also, different additives have been used with the objective of lowering down the densification temperature and to improve the mechanical and thermo-mechanical properties of such composites. PENA et al [19] studied the effect of MgO on zirconia–mullite composites and found that addition of small amount of magnesia increased the rate of densification by forming small amount of liquid phase. Similarly, titania lowered the sintering temperature of such composites by forming small amount of transient liquid phase [20]. Presence of CeO_2 enhanced the mullitization rate, stabilized tetragonal zirconia and increased fracture toughness of mullite−zirconia composites to 5.5−6 $\mathrm{MPa\cdot m^{1/2}}$ [21]. Addition of small amount of strontium oxide significantly improved the densification and it was found that 0.50% of SrO imparts optimum flexural strength and fracture toughness [22]. Dysprosia addition promoted densification of mullite–zirconia composites by forming liquid phase and it also formed solid–solution with zirconia and mullite, and 2.5% dysprosia containing

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composites showed the best mechanical properties [23]. DAS et al [24] studied the effect of yttria on reaction sintered mullite–zirconia composites from Indian coastal zircon flour and calcined alumina and concluded that yttria acted as solid solution additive and was more effective than any other additives because it does not form any low melting phases. La_2O_3 was used as sintering aid and it was found that the presence of lanthanum oxide decreased the densification temperature and significantly improved the thermal shock resistance of the mullite–zirconia composites [25]. Also, CaO as sintering aid was used in mullite–zirconia composites and it was reported that CaO lowered the densification temperature by forming transitory liquid phase [26]. But, the thermo–mechanical properties of such composites in the presence of CaO have rarely been reported.

In the present study, our aim is to synthesize mullite–zirconia composites by reaction sintering of zircon flour, sillimanite beach sand and calcined alumina in the presence of CaO. The effect of CaO on densification, microstructural characteristic and mechanical/thermo-mechanical properties of the resulting composites have been investigated.

2 Experimental

Raw materials selected for the present studies were zircon flour (Indian Rare Earth Limited), sillimanite beach sand (Trimax Industries, India) and calcined alumina (Hindalco, India). Chemical grade $Ca(OH)_2$ (Merck Specialties Private Limited, India) was used as sintering aid. Raw materials were characterized in terms of physico–chemical properties. Chemical analysis of all the raw materials was done by standard wet chemical methods. In our earlier investigation, we synthesized mullite−zirconia composites by varying amount of zirconia in mullite matrix via reaction sintering of zircon flour, sillimanite sand and calcined alumina. It was observed that 20% addition of zirconia in mullite matrix provided optimum mechanical and thermo-mechanical properties [27]. Therefore, four batch compositions containing 20% zirconia and 0, 4%, 8% and 12% of CaO with respect to zirconia were prepared (Table 1).

Table 1 Batch compositions with sample codes

Sample code	x(CaO) (with respect to ZrO_2)/%	x(Zircon flour)/%	x(Sillimanite sand)/%	x(Calcined alumina)/%
2Z	0	33.09	29.98	36.92
2Z4C	4	32.97	29.87	36.78
2Z8C	8	32.84	29.75	36.64
2Z12C	12	32.70	29.62	36.47

Raw materials were homogeneously mixed and ground by wet attrition milling for 4 h in zirconia pot using zirconia ball as grinding media in ethyl alcohol medium at the speed of 400 r/min. Resulting slurries were initially 24 h naturally dried followed by 24 h drying at (100±5) °C in an air oven. Dried masses thus obtained were crushed to break the agglomerate and passed through 150 μm sieve to get the desired powders. Resulting powders were uniformly mixed with 5% PVA (polyvinyl alcohol) solution as green binder and shaped into bars (size 75 mm × 5 mm × 5 mm) and pellets (size *d*20 mm × 10 mm) by uniaxially pressing at 45 MPa followed by the cold iso-static pressing at 140 MPa. Pressed samples were kept for 24 h natural drying subsequently 24 h drying in an air oven at temperatures of (100±5) °C.

Sintering of dried samples was done in programmable controlled electric furnace (Bysakh & Co., India) in the temperature range of 1450 to 1600 °C at the interval of 50 °C with 2 h soaking time at peak temperature. Firing schedule was maintained at a rate of 5 °C/min from room temperature to 1000 °C, followed by 3 °C/min up to the peak temperature. Sintered samples thus obtained were characterized in terms of various physical, mechanical, thermo-mechanical properties, phase and microstructural development. Apparent porosity (AP) and bulk density (BD) were measured by conventional water displacement method using Archimedes' principle (ASTM−C373−14). Phase development was studied by X-ray diffraction (XRD) technique. XRD patterns of the samples were collected over the Braggs' angle (2θ) between 10° to 80° by Philips X-ray diffractometer (model PW 1730) using nickel filtered Cu K_α radiation. To avoid the conversion of tetragonal to monoclinic zirconia during powder preparation, the sintered pellet samples (size *d* 20 mm × 2 mm) were used for XRD. Quantitative phase analysis of zirconia was done by the formula developed by GARVIE and NICHOLSON [28] using XRD patterns.

Mechanical and thermo-mechanical properties were measured using the bar samples sintered at 1600 °C (without additive) and 1550 °C (with additive). The flexural strength at room temperature was evaluated by three-point bending method (with a span of 40 mm and cross-head speed of 0.5 mm/min) using universal testing machines (model No. Instron 5500R) as per ASTM−C1161−13. Flexural strength at elevated temperatures (600, 900 and 1200 °C) was also measured by three-point bending method as per ASTM−C1211−13. Fracture toughnesses of the samples were calculated by Vicker's indentation method [29], applying 3 kg load with 15 s dwell time on the very fine polished surface (1 μm surface finish).

Reversible linear thermal change of the samples during heating–cooling cycles was done on dilatometer (model No. NETZSCH DIL 402C). For this purpose, sintered samples with dimensions of *d*8 mm × 25 mm were used. Thermal shock resistances of the sintered bar samples were measured in terms of retained flexural strength after 5, 10 and 15 thermal shock cycles as per ASTM−C1171−05. Thermal shock was given to the samples from 1200 °C to ambient temperature in a raising hearth furnace by keeping 10 min inside the furnace at 1200 °C and then 10 min air quenched at ambient temperature. Microstructural evaluation was done by SEM (Supra™ 35VP, Carl Zeiss) using polished, thermally etched and carbon coated samples. Grain sizes of the composites were determined by ImageJ software using SEM (scanning electron microscopy) images. Elemental analysis of the different phases/grains was done by energy dispersive X-ray (EDAX) during the SEM observation.

3 Results and discussion

3.1 Raw materials characterization

Chemical analyses of raw materials are shown in Table 2. Zircon flour contains 59.74% ZrO_2 and 31.94% SiO_2 as its major constituents with CaO and alumina as main impurities. Sillimanite beach sand contains 59.87% Al_2O_3 and 38.57% SiO_2. Alumina content in calcined alumina is 99.54%. XRD patterns of raw materials are represented in Fig. 1. Zircon is the major crystalline phase present in zircon flour. SiO_2 content is higher than the stoichiometry amount of sillimanite and free silica appears as quartz. Corundum is the only crystalline phase present in calcined alumina.

Table 2 Chemical analyses of raw materials (mass fraction, %)

Chemical constituent	Zircon flour	Sillimanite sand	Calcined alumina
ZrO_2	59.74	−	−
SiO_2	31.94	38.57	0.017
Al_2O_3	6.76	59.87	99.54
Fe_2O_3	0.17	0.40	0.017
TiO_2	Trace	0.07	−
CaO	1.03	−	−
Na_2O	0.07	0.40	0.40
K_2O	Trace	0.09	−
MgO	Trace	−	−
HfO_2	0.03	−	−

3.2 Densification

Densification is an essential parameter for characterization of any ceramic product. It is generally manifested in terms of decrease in apparent porosity (AP) and increase in bulk density (BD). Variation in apparent porosity and bulk density of the sintered samples with sintering temperature and lime content has been shown in Fig. 2. It can be seen that densification rate of the samples containing additive is higher than that of the sample without additive. All samples with additive have achieved almost nil apparent porosity and optimum bulk density at 1550 °C, whereas samples without additive have attained the same level of densification at higher temperature (1600 °C). Samples having 12% CaO with respect to zirconia (2Z12C) have achieved almost nil apparent porosity at 1450 °C, whereas samples 2Z (without CaO) have around 30% of apparent porosity. In the ZrO_2−Al_2O_3−SiO_2−CaO quaternary system, the formation of anorthite ($CaAl_2Si_2O_8$) phase occurred at 1440 °C [26,30]. However, in the present case, presence of CaO also forms small amount of transitory liquid phase (calcium aluminosilicate) to facilitate sintering, which was confirmed by EDAX analysis of the sample.

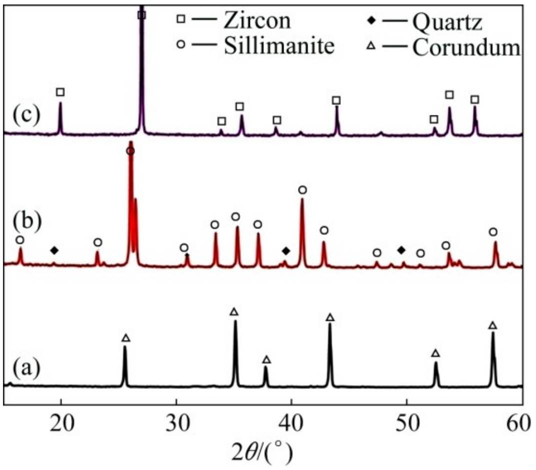

Fig. 1 XRD patterns of raw materials: (a) Calcined alumina; (b) Sillimanite sand; (c) Zircon flour

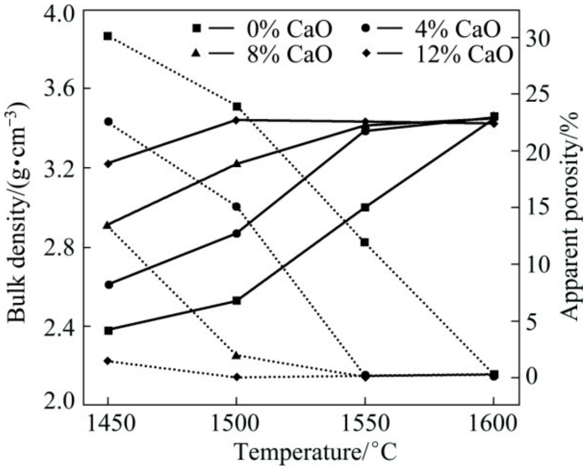

Fig. 2 Variation in bulk density (solid line) and apparent porosity (dash line) of sintered samples with sintering temperature

3.3 Chemical reactions and phase development

Sillimanite beach sand converts into mullite and amorphous silica [17] on heating. Similarly, zircon flour decomposes into zirconia and silica after heat treatment and yields the source of zirconia. Released silica again reacts with calcined alumina to form stoichiometric mullite. XRD patterns of the samples sintered at 1550 °C have been illustrated in Fig. 3. In all samples, three major phases are identified: mullite, tetragonal zirconia (Z_t) and monoclinic zirconia (Z_m). Relative peak intensity of Z_t increases and consequently peak intensity of Z_m decreases with the addition of CaO; which confirms the stabilization of tetragonal zirconia at room temperature with increase of CaO content.

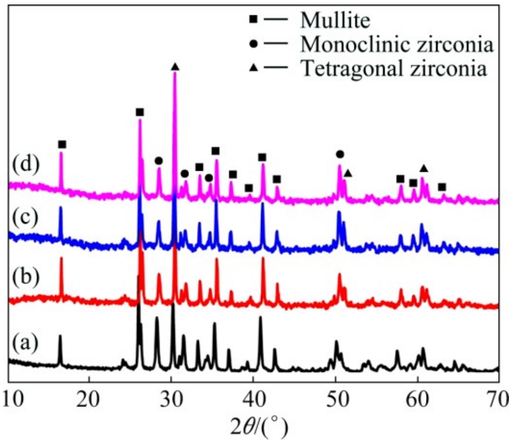

Fig. 3 XRD patterns of samples sintered at 1550 °C: (a) 2Z; (b) 2Z4C; (c) 2Z8C; (d) 2Z12C

Quantitative information of relative zirconia content of the samples has been shown in Table 3. It can be seen that relative Z_t contents of the samples are increased with increase in the CaO content from 0 to 8%. Afterwards, further addition of CaO from 8% to 12% has not any significant effect on stabilization of Z_t.

Table 3 Room temperature mechanical properties of different samples

Sample	Sintering temperature/ °C	Relative Z_t/%	Flexural strength /MPa	Fracture toughness/ (MPa·m$^{1/2}$)
2Z	1600	38.00	231.33±15.33	5.69±0.49
2Z4C	1550	56.93	225.28±15.78	6.19±0.31
2Z8C	1550	64.01	221.82±16.04	6.45±0.91
2Z12C	1550	62.36	214.88±12.34	5.49±0.43

3.4 Reversible linear thermal change

Reversible linear thermal change of the samples during heating–cooling cycle is represented in Fig. 4. During heating−cooling cycles, the conversion of Z_m to Z_t (on heating) and vice versa (during cooling) forms hysteresis area due to change in volume. The changes in the area of hysteresis loop provide qualitative information regarding the stabilization of zirconia. It can be observed that hysteresis area is decreasing with increase in CaO content, which confirms the stabilization of zirconia.

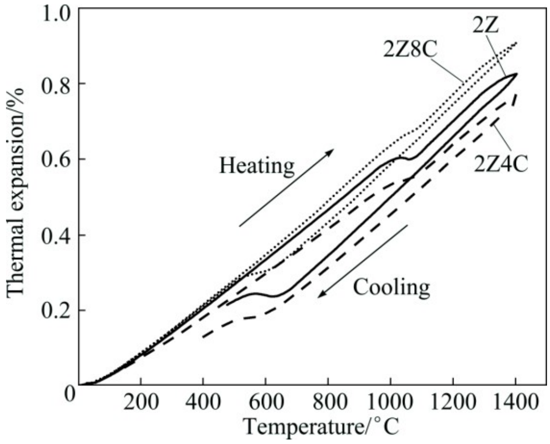

Fig. 4 Reversible linear thermal change of samples sintered at 1550 °C during heating–cooling cycle

3.5 Microstructure and EDAX

Scanning electron photomicrographs of the samples are shown in Figs. 5((a)–(d)). Two clearly distinguished phases, mullite (dark grains) and zirconia (bright grains) appear in the micrographs along with some close pores. Spot analysis of magnified SEM image of the sample containing 2Z12C reveals the formation of calcium−aluminosilicate phase across intergranular grain boundaries (Fig. 6). Average grain size of the composites is summarized in Table 4. Average grain size of the sample 2Z (without additive) is 2.10 μm, which reduces to 1.78 μm with the addition of 4% CaO. It is quite obvious, as samples without additive have sintered at relatively lower temperature (1550 °C). But, as the CaO content has increased from 4% to 12%, the average grain size has increased to 2.61 μm (sample 2Z12C). This can be attributed to the presence of higher amount of CaO which favors densification at earlier temperature, so further increase in the sintering temperature causes grain growth of the samples [24].

3.6 Mechanical and thermo-mechanical properties

Samples sintered at 1600 °C (without additive) and 1550 °C (with additive), as samples with additives have achieved optimum densification at 1550 °C, are selected for mechanical and thermo-mechanical properties evaluation. Room temperature mechanical properties of different samples are represented in Table 3. Sample 2Z (without additive) have shown flexural strength of 231.33 MPa and fracture toughness of 5.69 MPa·m$^{1/2}$. However, with addition of CaO, slight improvement in

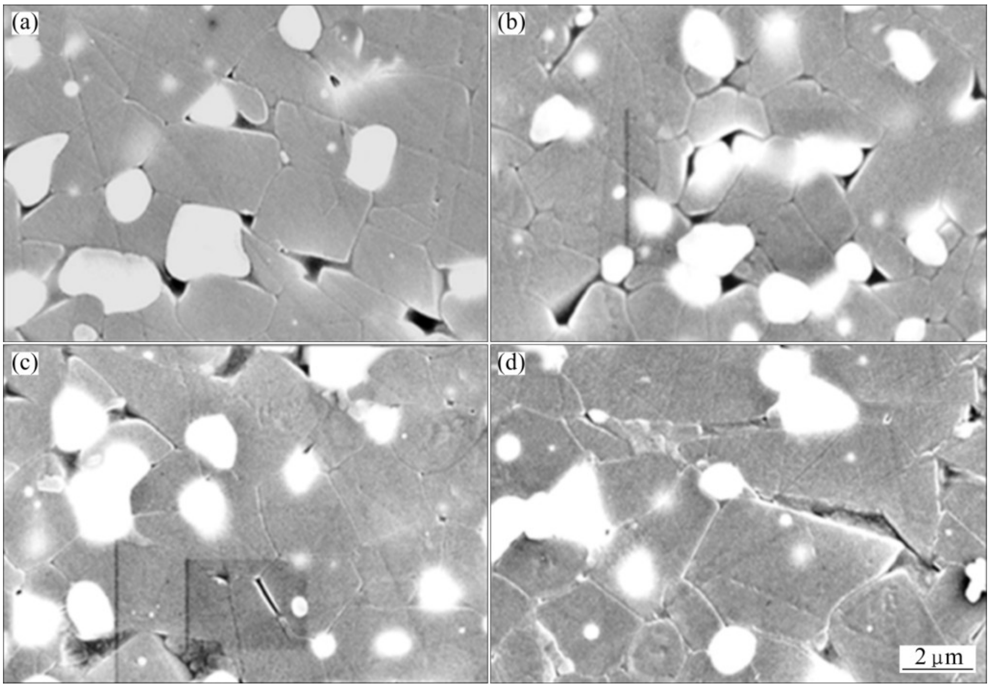

Fig. 5 SEM photomicrographs of polished, thermally etched and carbon coated surfface of samples: (a) 2Z; (b) 2Z4C; (c) 2Z8C; (d) 2Z12C

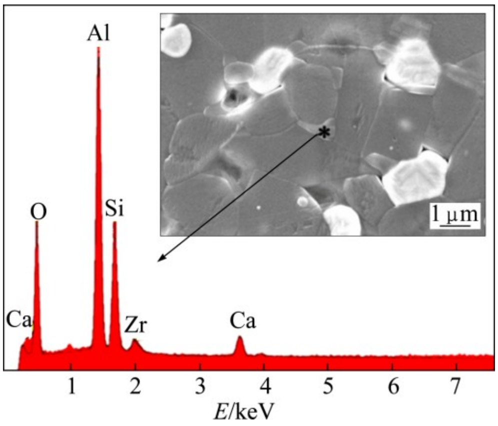

Fig. 6 Magnified SEM image and spot analysis of sample 2Z12C sintered at 1550 °C

Table 4 Average grain sizes of different samples

Sample	Sintering temperature/°C	Average grain size of composite/μm
2Z	1600	2.10
2Z4C	1550	1.78
2Z8C	1550	2.26
2Z12C	1550	2.61

fracture toughness has been observed with very minor reduction in room temperature flexural strength. Samples with 4% CaO exhibited 225.28 MPa of flexural strength and fracture toughness of 6.19 MPa·$m^{1/2}$. With further addition of CaO (8%), the fracture toughness increases to 6.45 MPa·$m^{1/2}$. Presence of CaO stabilizes tetragonal zirconia, which keeps the matrix strained. As the cracks propagate, tetragonal to monoclinic zirconia phase transformation takes place, which is associated with 4%−5% volume increase and generates shear strains. These together absorb the crack propagation energy, and thus increase the fracture surface energy, as a result fracture toughness increases [31].

Variation of high temperature flexural strength of the samples with different CaO contents as a function of temperature is shown in Fig. 7. All samples have shown almost similar variation in flexural strength with temperature. Initially, flexural strength is decreasing till 900 °C. This decrement in strength is due to elastic bond relaxation [32]. Afterwards, the flexural strength increases

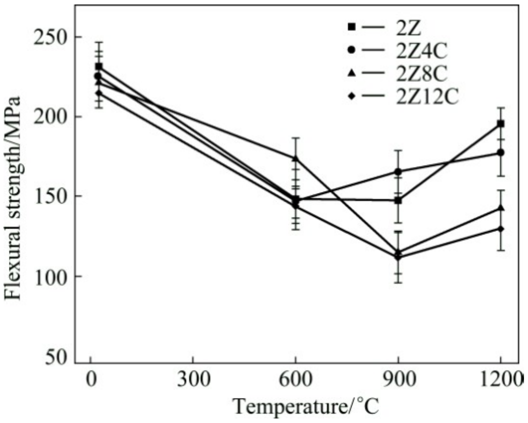

Fig. 7 Variation in flexural strength of samples sintered at 1600 °C (without CaO) and 1550 °C (with CaO) with temperature

with the temperature (from 900 °C to 1200 °C) due to healing of the critical cracks by highly viscous glassy phases [33]. It can be seen that samples with and without additives have shown nearly the same flexural strength at room temperature, samples with additive have shown slightly lower flexural strength at elevated temperature due to presence of liquid phase across grain boundaries (Fig. 6).

Variation of flexural strength of the sintered samples with the number of air quenched cycle has been shown in Fig. 8. Initially, retained flexural strength of all the samples has decreased (till 5 thermal shock cycles); afterwards, the change in flexural strength is almost constant. Samples without additive (2Z) have retained only ~20% of its initial flexural strength after 5 cycles. Incorporation of CaO has significantly improved the thermal shock resistance of material. Samples with 4% CaO (2Z4C) show better thermal shock resistance compared with other samples, as it has retained around 64% of its initial flexural strength even after 15 thermal shock cycles. This improvement in strength is attributed to the stabilization of zirconia by CaO, as partially stabilized zirconia has good thermal shock resistance [34]. Also, the thermal shock resistance of the samples can be improved by the decrease in grain size [35]. The average grain size of the composites with 4% CaO (2Z4C) has decreased (Table 4), which further improves the thermal shock resistance of the samples, since grain boundaries act as a crack arrestors. This is also correlated to the thermal expansion/contraction mismatch among the phases like mullite, monoclinic zirconia and tetragonal zirconia (due to difference in their coefficient of thermal expansions) and zirconia phase transformation generates microcracks, which has advantageous effects on thermal shock resistance [36].

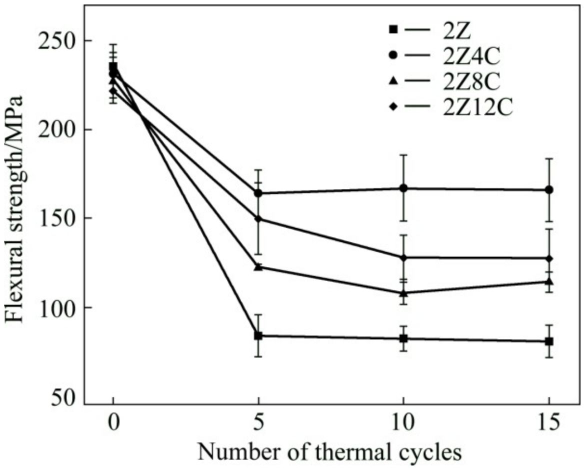

Fig. 8 Retained flexural strength of samples sintered at 1600 °C (without CaO) and 1550 °C (with CaO) after 0, 5, 10 and 15 thermal cycles (air quenched) from 1200 °C to ambient temperature

4 Conclusions

Reaction sintering of zircon flour, sillimanite beach sand and calcined alumina can be a better alternate to preparation of mullite–zirconia composites. Presence of CaO as sintering aid increased the rate of densification and formed dense composites at lower temperature of 1550 °C. Samples with 4% CaO have shown flexural strength of ~225 MPa and fracture toughness of ~6 MPa·m$^{1/2}$ at room temperature. Also, CaO stabilized the tetragonal zirconia phase and improved the thermal shock resistance. Samples with 4% CaO (2Z4C) retained around 64% of its initial flexural strength even after 15 thermal shock cycles.

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氧化钙对锆石和硅线石海滩砂反应烧结制备莫来石−氧化锆复合材料热力性能的影响

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摘　要：采用印度沿海锆石粉与硅线石海滩砂反应烧结，制备含 20%(质量分数)氧化锆的莫来石−氧化锆复合材料。添加 4%~12%(摩尔分数)的氧化钙作为添加剂。研究了添加剂对压实性能、显微组织、力学性能和热力性能的影响。添加氧化钙可以使压实温度从 1600 °C 降低至 1550 °C。氧化钙可以形成少量的液相(铝硅酸钙)，有利于烧结进行。添加 4%氧化钙可使复合材料的晶粒尺寸减小，当添加量大于 4%时，材料的晶粒尺寸随氧化钙添加量的增加而增大。添加 4%氧化钙样品的弯曲强度约为 225 MPa，断裂韧度约为 6 MPa·m$^{1/2}$，且抗热冲击性能得到明显提高。氧化钙可以稳定四方氧化锆，从而提高材料的力学性能。

关键词：反应烧结；莫来石−氧化锆复合材料；弯曲性能；耐火材料

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