The role of kyanite in the crystallization and densification of the high strength mullite matrix composites

Microstructure and mechanical properties

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Abstract The crystal structure, the unit cell parameters and the extent of mullitization were determined, using the Rietveld method, for range of mullite matrix formulations in which kyanite is used as particles reinforcement. The results combined with the mechanical properties and microstructure indicated the effectiveness of the kyanite particles to enhance the strength (>200 MPa), the Vickers hardness (>11 GPa) and the elastic modulus (150 GPa). The strengthening mechanism was particularly linked action of particles reinforcement. At low temperature, kyanite acts as fillers reducing the porosity and playing the role of nucleation sites for the crystallization of metakaolin to mullite. At high temperature (>1350 °C), kyanite decomposes to mullite avoiding the grain growth of the existing crystals and delaying the densification. The extent of the reduction in porosity and the extreme limitation of the liquid phase ensure the homogeneity and the refractoriness that justify the strength enhancement. The unit cell parameters and the crystal structure confirmed predominance of the mullite 3:2 with their small grain size being one of the most stable mullite phases. The small size of their particles and the continuity into the mullite matrix composites allow good packing process for the optimum characteristics achieved: strength, microstructure and thermal expansion coefficient.

Keywords Kyanite · Mullite · Microstructure · Vickers hardness · Elastic modulus · Grain growth

Introduction

Mullite matrix composite with good densification and interlocked microstructure presents enhanced mechanical properties including the flexural strength, hardness and elastic modulus. To produce such a matrix, researchers generally used particular processing technology that requires high cost and energy [1–5] or particles reinforcement as silicon-carbide, zirconia, α-Al2O3, etc. preparation of which usually required very high cost conducing to a final product with very high global warming potential (GWP) [6, 7].

The challenge for the ceramist today is to propose traditional and advanced materials like mullite matrix composite that results from a highly sustainable raw materials and process. The simplest process for mullite production remains the use of solid-state sintering with kaolin as principal raw material. Appropriate particle reinforcement capable to enhance the mechanical properties while maintaining the continuity of the microstructure for a final matrix that can withstand thermal shock cycles, microcracks (interfacial), creeps, etc. is needed. In this study, we investigate the effects of kyanite as particle reinforcement of mullite matrix into the microstructure, densification and mechanical behaviour. The thermo-elastic properties of kyanite-based ceramics have been investigated and their
thermal expansion behaviour elucidated [8, 9]. However, kyanite as 100 mass% raw materials is not convenient for the optimum thermo-mechanical cycles of refractory composites due the extensive expansion [8, 9]. To improve the quality of the mullite matrix composite, nucleating agents as Fe and Ti are also used [10, 11]. The grain size and the densification of mullite matrix composite depend not only on firing temperature and time. Particularly, the formulation design is significant in determining the final microstructure. The shape of the mullite crystals is always elongated especially when kyanite is nucleated from liquid phase [10].

The particles reinforcements are used in general with the aim to develop interlocking network, providing difference in thermal expansion coefficients between phases which in turn produces a compressive stress on the most expanded one. The increase in the mechanical properties that results from the particles reinforcement is found from the formation of microcomposite microstructure where the particles reinforcement enhances densification, reduces porosity inducing deflection of the crack path along the particle–matrix interfaces. The matrix interfaces and the final microstructure in the mullite matrix composite will govern the stability and the durability through the life cycle. Creep into polycrystalline mullite at high temperature is controlled by diffusion, but smaller volume of the final microstructure in the mullite matrix composite will govern the stability and the durability through the life cycle. Creep into polycrystalline mullite at high temperature is controlled by diffusion, but smaller volume of grain boundary glass increases the creep rate as compared to a pure mullite ceramic. Grain boundary sliding, facilitated by softening of the intergranular glass, dominates creep behaviour.

Kyanite has been used to produce viscoelastically toughened mullite through thermally assisted assembled deposition. The viscoelasticity results from the residual SiO2 obtained after the transformation to mullite. Lamellar structures of 3Al2O3·2SiO2 are described from the decomposition of kyanite [12]. At elevated temperature, tabular grains with rounded edges are observed [12]. Rahbar et al. [13] described the formation of viscous bridging ligament responsible for the improvement of the cracks nucleation and growth in mullite matrix composite from kyanite. Although the presence of silica coating needle-like mullite grains is the reason proposed to avoid the growth of mullite grains during the decomposition of the kyanite at high temperature, matrices from kyanite as the only raw materials result to high volume expansion [8, 9, 12, 13]. The microstructure and mechanical properties (including flexural strength, hardness and elastic modulus) are used together with the pore size distribution to assess the efficiency of the metakaolin-metabauxite-kyanite system as new mullite matrix composite formulations for high temperature refractory composites.

### Experimental procedures

#### Materials

**Starting pastes and forming of green compacts**

The formulations KY3, KY4 and KY5 were designed by adding the calcined bauxite to metakaolin in the way to have the theoretical chemical composition of mullite, 3Al2O3·2SiO2. The basic formulation received 37.5, 42.5 and 50 mass% of fine (φ < 60 μm) powder of kyanite as reinforcement. The final chemical composition of the three formulations is summarized in Tables 1 and 2. The three green compacts: KY3, KY4 and KY5 were designed using metakaolin, calcined bauxite and kyanite in the way to reduce the residual silica that generally is at the origin of the viscous glassy responsible for the decrease in strength at high temperature for the mullite matrix composites. The metakaolin was prepared through the calcination, at 700 °C for 4 h, of a standard kaolin from Mayoum, Cameroon [14]. The calcined Kaolin presents 51.61 mass% of SiO2, 39.42 mass% of Al2O3, 1.94 mass% of Fe2O3, 0.95 mass% of K2O and 5.12 mass% of TiO2 as analysed using the inductively coupled plasma mass spectrometry (ICP-MS). Bauxite was collected from Danielle bauxite plains, Tchabal-Haleo sector in Mini Martap, main village of Adamawa Region, Cameroon [15]. Kyanite was collected from Makak in the Central Region of Cameroon. Bauxite was calcined at 700 °C for 4 h having final bulk composition with 0.655 mass% of SiO2, 91.14 mass% of Al2O3, 5.41 mass% of TiO2 and 2.13 mass% of Fe2O3. 58.40 mass% of Al2O3 and 36.87 mass% of SiO2 were found in Kyanite. Suitable proportion of metakaolin, metabauxite and kyanite were mixed and wet and ball-milled for 60 min in rapid ball-mill, 1200 rpm. The paste obtained was dried at room temperature up to have the powder that can be pressed using pressure (20 MPa) in uniaxial hydraulic press. The hydraulic press is equipped with steel moulds suitable for the production of disc specimens. Disc compacts (40 mm (φ) × 10 mm (h)) were produced. The specimens were dried at room temperature in laboratory up to constant then the drying is concluded in oven at 110 °C for 24 h before thermal analysis and firing.

#### Table 1 Composition of the used raw materials (metakaolinite, metabauxite and kyanite)

| Material       | Al2O3 | SiO2 | TiO2 | Fe2O3 | K2O | LOI |
|----------------|-------|------|------|-------|-----|-----|
| Metakaolin     | 39.42 | 51.61| 5.12 | 1.94  | 0.95 | 0.96|
| Metabauxite    | 91.14 | 0.655| 5.41 | 2.13  | –   | 0.665|
| Kyanite        | 58.40 | 36.87| –    | 3.054 | –   | 1.676|
Table 2 Percentage of any one in the three formulations

|       | Metakaolin | Metabauxite | Kyanite |
|-------|------------|-------------|---------|
| PK3   | 42.5       | 20          | 37.5    |
| PK4   | 37.5       | 20          | 42.5    |
| PK5   | 30         | 20          | 50      |

Thermal expansion behaviour

Thermal behaviour (Thermal Expansion-TE, Thermal Expansion Coefficient-CTE and the derivative of the shrinkage-dl/lo) of the fired samples of mullite matrix composites (KY3, KY4 and KY5) was studied using the horizontal optical dilatometer Misura® ODLT. The procedure of non-contact and no interference makes the ODLT the most innovative instrument of thermal analysis. The double beam optical dilatometer is designed to reach up to 1750 °C. The specimens of 5 × 5 × 15 mm were used. The resolution dt.dl was 0.1 °C 478 nm. The accuracy in x is 0.05 × 10⁻⁶. The measurement was performed at 10 °C/min for all the samples.

Characterization of the fired specimens of mullite matrix composites

XRD

X-ray powder diffraction (XRPD) data were collected using a θ/θ diffractometer (PANalytical, CuKα radiation), equipped with a real-time multiple strip (RTMS) detector that allows fast data acquisition. The incident beam pathway included a soller slit (0.04 rad) as well as divergence and anti-scattering slits (both with an opening of 0.5°). The diffracted beam passed through a Ni filter, a soller slit (0.04 rad) and an antiscatter blade (5 mm). A virtual step scan (0.0167 °2θ) was performed in the range 3–90 °2θ.

Full quantitative phase analyses (FQPA) were performed using XRPD data and Rietveld refinements. The software used were GSAS (software package) [16], and its graphical interface EXPGUI (interface to perform Rietveld analysis) [17]. XRPD data were collected using dry sample powders mixed with a known amount of Silicon (10 mass% NIST 640c) as internal standard which allowed to accurately quantify the crystalline phases as well as the amorphous fraction composing the sample (the latter including crystalline phases under the detection limit) as described in detail in previous work [18]. The crystallinity of the internal standard determined by others [19] was accounted for when calculating the real weight fractions [18]. In addition, by fixing the unit cell of the standard to certified values in the Rietveld refinements, the zero offset as well as sample displacement were corrected, thus allowing to determine accurate unit cell parameters of the crystalline phases in the sample [20].

Mercury intrusion porosimetry

One important aspect of the microstructure of ceramics and refractories is the porosity. The interconnected, open pore size distribution in a porous material is most easily assessed using the technique of mercury intrusion porosimetry (MIP) in which a holder is partially filled with weighed, dried sample, evacuated and filled Hg. An Autopore IV 9500, 33,000 mercury intrusion porosimeter (MIP) covering the pore diameter range from approximatively 360–0.005 μm having two low-pressure ports and one high-pressure chamber was used for the pores analysis. Pieces prepared from the bulk of each sample with specimens of ~1 cm³ of volume for the MIP.

Mechanical properties and microstructure

The bi-axial bending strength of the mullite matrix composites was measured by the piston-on-three-balls test method. The piston-on-three-balls have the advantage in the tolerance for specimen warpage [21, 22]. The specimens were prepared with (R – a) = 0.65 t, R and t being the radius and the thickness of the specimen, respectively, and a is the radius of the loading piston. The test was performed using a Mechanical Testing Machine (MTS 810, USA), and the maximum stress was evaluated from the failure load P as [21]:

\[ \sigma_{\text{max}} = \frac{3PL}{4R^2 (1+\nu)(1-\nu)(1-\nu)} \]

where b is the radius of the circle formed by the supporting balls and \( \nu \) the Poisson’s ratio (considered equal to 0.21). The pieces of mullite matrix specimens were collected after the mechanical test and used for the preparation of powders for X-ray Diffraction (XRD), the scanning electronic microscope (SEM) and the microindentation.

Vickers microhardness, Hv (GPa), measurements were performed using the indentation technique at maximum load of 1 N with an approach speed of 1.5 N min⁻¹. The samples used for indentation analysis were prepared with the same method with those used for SEM analysis without etching. The depth range was 100 μm. For each experiment, 27 indentations were performed and the results statically analysed in the aim to understand the influence of microheterogeneity on the mechanical properties of fired mullite matrix composites. Analysis was performed using CSM instruments: indenter coupled to a microcamera and software for image elaboration and analysis of indentations. The elasticity Young’s modulus, E (GPa), was
calculated automatically for each indentation by the software from the Hv/E ratio, applying the equation given by Marshal et al. [23].

The microstructure of fired specimens of mullite matrix composites was studied by Environmental Scanning Electron Microscope ESEM Quanta-200, Oxford Instruments. Fractured and polished specimens were used for each sample. The polished specimens were etched in 5% HF-HNO₃ solution for 30 s for crystalline phase identification. All the specimens for SEM analysis were mounted on aluminium stubs and sputter-coated with 10 nm of Au/Pd. The microanalysis was performed using EDS (X_EDS INCA, Oxford Inst.). For each formulation, both etched and non-etched specimens were used for the ESEM analysis with the objective to ascertain on the extent for glassy phase formation.

**Results and discussion**

**Mullitization**

The data on the evolution of the crystalline and amorphous content of KY3, KY4 and KY5 with the temperature between 1250 and 1550 °C are described to Fig. 1. Up to 1250 °C, the matrices are still dominated with corundum, kyanite and amorphous phases with only 27.7, 23.8 and 23.4% of mullite in KY3, KY4 and KY5, respectively. Between 1250 and 1350 °C, the amount of amorphous remained high (>15.3%) for all the three matrices although the increase in mullite formation. In fact, mullite increased from 27.7 to 34.9% in KY3, 23.8–54.9% and 23.4–45.7% in KY4 and KY5, respectively. In the meantime, the kyanite decreased to zero and the amount of the corundum remained without significant change (Fig. 1). It can be suggested that the mullite present into the matrices up to 1250 °C is essentially that from the transformation of metakaolin [24–26]. The amorphous phase identified includes metastable alumina and mullite as well as amorphous silica. The increase in temperature between 1350 and 1450 °C conducted to 72% of mullite in KY3 and only 68% in KY4 and KY5. The corundum decreased from 23.6 to 10.1% in KY3, while the amorphous content decreased to 15%. A new class of mullite that obviously is from the reaction between amorphous silica and corundum (or metastable alumina) constitutes part of the 72 and 68% observed. Between 1450 and 1550 °C, the mullite content increased to 78.8% in KY3, while corundum is reduced to 2.1% but with a slight increase in amorphous phase from 15.5 to 17.2%. This increase in amorphous was accompanied by a densification and may resulted from the liquid film formed from the amorphous matters. In the KY3 formulation, the relative low amount of kyanite particles make metakaolin remained the main solid precursor with significant residual silica that remained after transformation of metakaolin to mullite. For the KY4 and KY5, the increase in mullite formation was continuing from 1250 to 1550 °C. Temperature at which there was still decrease of amorphous phase and corundum. Almost 80% of mullite was obtained with 2% of corundum at 1550 °C. The amorphous
phase of >15% was found to not be a liquid phase suggesting that the densification and mullitization in those matrices were still ongoing. This is in agreement with the refractoriness of the mullite matrix composite from both systems. In fact the low density of the matrix together with the reduced shrinkage allow the increase in the refractoriness of the kyanite-based mullite matrix composite in the range of composition KY4 and KY5. The step of decomposition of kyanite is correlated with a relative increase in volume of voids and the reduction in the intimated contact that is necessary between particles for the thermo-chemical reaction/transformation. By the way, the mullitization-densification was delayed as the kyanite content increased (Fig. 2). Increasing the kyanite content in the range of the formulations investigated, the remaining silica available into the matrix after the complete mullitization is reduced conducing to a reduction in the probability of having viscous liquid phase. This delays the densification and improves the refractory behaviour.

The variation of the coefficient of the thermal expansion obtained from the dilatometry curves of KY3, KY4 and KY5 for the specimens initially treated at 1450 and 1550 °C are shown in Fig. 3. For the specimens treated at 1450 °C, only KY3 has the matrix stable thermically. KY4 and KY5 with the increasing amount of kyanite showed significant instability with thermo-chemical activity of the matrices. Particularly, the specimen of KY5 showed important variation of the thermo-chemical activity as from 1000 °C (6000 s). Around 1350 °C, the expansion coefficient increased first then decreased again before a stabilized contraction between 1400 and 1450 °C and further expansion at higher temperature. This behaviour of specimens KY5 in this range of temperature can be easily correlated to the hypothesis of the delay of mullitization-densification with the increase in kyanite content for the range of formulations under study. The thermo-chemical activity of KY5 at high temperature is linked to that of the remaining components as amorphous silica, metastable alumina or amorphous mullite with their possible reactivity that seems to go beyond 1550 °C. The thermal expansion coefficient which is 5.92, 5.15 and 6.92 × 10⁻⁶/°C for KY3, KY4 and KY5 between 200 and 1000 °C decreased to 5.27, 3.75 and 4.67 × 10⁻⁶/°C between 1000 and 1550 °C for the specimens initially treated at 1450 °C. For the specimens initially treated at 1550 °C, the thermo-chemical activity of all the samples is evidenced with significant reduction in the thermal

Fig. 2 XRD Patterns illustrated the refinement by Rietveld method: a Optimum densified matrix of KY3 at 1550 °C, b incomplete mullitization of KY5 at 1550 °C

Fig. 3 Variation of the Thermal expansion Coefficient with temperature: a samples treated initially at 1450 °C and b samples treated initially at 1550 °C
expansion coefficient. Values of $a = 4.87, 5.65$ and $5.85 \times 10^{-6}/\degree\text{C}$ is obtained between 200 and 1000 $\degree\text{C}$. Values that increased to $6.11, 6.68$ and $7.06 \times 10^{-6}/\degree\text{C}$ between 1000 and 1550 $\degree\text{C}$. In the range of temperature $[1500, 2000]$ $\degree\text{C}$, both samples initially treated at 1450 or at 1550 $\degree\text{C}$ showed an increase in the thermal expansion coefficient which can be explain with the viscoelastic behaviour of the kyanite-based mullite matrix composites [12, 13]. The thermally assisted decomposition of kyanite, sillimanite and andalusite produces viscoelastically toughened ceramics [13]. These are minerals with the same chemical formula ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$), but different crystal structures. Upon heating, they decompose into mullite ($3\text{Al}_2\text{O}_3\cdot\text{2SiO}_2$) and $\text{SiO}_2$, and the structures in which $\text{SiO}_2$ can provide viscoelastic toughening. Furthermore, most natural deposits of kyanite contain ($\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$) that can give rise to improved levels of viscoelastic crack bridging. At low temperature, the thermal behaviour of mullite matrix composites seems to be generally uniform with similar behaviour. At high temperature, the behaviour of the matrices is becoming linked to their thermal history, the bulk chemical composition and final microstructure. In the range of the formulations under investigation, the presence of kyanite reduces amount of the residual silica after the formation of mullite and ability of the silica from kyanite decomposition to promote viscoelasticity give a particularity to the thermal behaviour and properties of mullite matrix composites as strength and microstructure.

Table 3  Refined unit cell parameters and stoichiometry of mullite (mol% $\text{Al}_2\text{O}_3$) crystallized at various temperatures from the base composition KY3

| $T^\circ\text{C}$ | Unit cell parameters/Å | $\text{Al}_2\text{O}_3$/mol%$^a$ |
|-------------------|------------------------|-------------------------------|
|                   | $a$        | $b$       | $c$       | $V$       |                          |
| 1250              | 7.547 (1) | 7.701 (1) | 2.8907 (3) | 168.02 (2) | 61.0 (2)  |
| 1350              | 7.552 (1) | 7.702 (1) | 2.8908 (3) | 168.13 (2) | 61.6 (2)  |
| 1450              | 7.5514 (2) | 7.7001 (2) | 2.89044 (6) | 168.069 (6) | 61.61 (3) |
| 1550              | 7.5529 (2) | 7.6975 (1) | 2.88928 (5) | 167.979 (5) | 61.82 (3) |
| $^a$ Calculated from the refined a-axis length as described by Ban and Okada [28] |

Table 4  Refined unit cell parameters and stoichiometry of mullite (mol% $\text{Al}_2\text{O}_3$) crystallized at various temperatures from the base composition KY4

| $T^\circ\text{C}$ | Unit cell parameters/Å | $\text{Al}_2\text{O}_3$/mol%$^a$ |
|-------------------|------------------------|-------------------------------|
|                   | $a$        | $b$       | $c$       | $V$       |                          |
| 1250              | 7.545 (1) | 7.702 (1) | 2.8930 (4) | 168.10 (3) | 60.7 (2)  |
| 1350              | 7.5487 (3) | 7.7008 (3) | 2.8887 (1) | 167.922 (9) | 61.22 (4) |
| 1450              | 7.5497 (2) | 7.7004 (2) | 2.88988 (6) | 168.006 (5) | 61.36 (3) |
| 1550              | 7.5525 (1) | 7.6975 (1) | 2.88938 (5) | 167.977 (5) | 61.77 (1) |
| $^a$ Calculated from the refined a-axis length as described by Ban and Okada [28] |

Table 5  Refined unit cell parameters and stoichiometry of mullite (mol% $\text{Al}_2\text{O}_3$) crystallized at various temperatures from the base composition KY5

| $T^\circ\text{C}$ | Unit cell parameters/Å | $\text{Al}_2\text{O}_3$/mol%$^a$ |
|-------------------|------------------------|-------------------------------|
|                   | $a$        | $b$       | $c$       | $V$       |                          |
| 1250              | 7.544 (1) | 7.704 (1) | 2.8909 (4) | 168.02 (3) | 60.5 (2)  |
| 1350              | 7.5488 (5) | 7.7008 (6) | 2.8889 (2) | 167.94 (1) | 61.23 (7) |
| 1450              | 7.5483 (2) | 7.6998 (2) | 2.88924 (6) | 167.922 (6) | 61.16 (3) |
| 1550              | 7.5518 (1) | 7.6975 (1) | 2.88924 (5) | 167.952 (5) | 61.66 (1) |
| $^a$ Calculated from the refined a-axis length as described by Ban and Okada [28] |
The crystal structure of mullite is orthorhombic, with average chemical formula that may range from $3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2$ (3:2) to $3\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ (2:1) [27]. The mullite phase boundaries join at $1890^\circ\text{C}$ with a composition of 77.2 mass% $\text{Al}_2\text{O}_3$, which corresponds to $2\text{Al}_2\text{O}_3$ (2/1-mullite). With decreasing temperature, the composition of mullite shifts towards lower $\text{Al}_2\text{O}_3$ contents. Below about $1600^\circ\text{C}$, the mean $\text{Al}_2\text{O}_3$ content of mullite is <73 mass%, corresponding to a composition of about $3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2$ (3/2-mullite). 2/1- mullite with needle-like crystals form presents low mechanical properties than 3/2-mullite. The octahedral $\text{AlO}_6$ clusters which form the columnar structure by sharing edges, and the centre of the orthorhombic unit cell do not change during the rearrangement necessary according to the exact chemical formula (level of removal of bridging O(C) oxygen atoms with formation of oxygen vacancies). The elemental formula of mullite in this well-accepted defect structure is expressed as $\text{Al}_{2+x}^{\text{VI}}(\text{Al}_{2+2x}^{\text{IV}}\text{Si}_{2-2x})\text{O}_{10-x}$ where $x$ denotes the amount of missing oxygen from the formula and VI and IV denote six fold and four fold coordination’s of aluminium, respectively, and silicon occupies the fourfold positions [27, 28]. Tables 3–5 show the refined unit cell parameters and the stoichiometry of mullite (mol% $\text{Al}_2\text{O}_3$) crystallized at various temperatures for the formulations KY3, KY4 and KY5. The parameter $a$ is 7.547 Å for all the samples at $1250^\circ\text{C}$. Increasing the temperature, the value of 7.552 Å is obtained for KY3 up to $1550^\circ\text{C}$. For KY4 and KY5, the increase in the value of a parameter was not as significant and remains from 7.548(2) Å up to $1450^\circ\text{C}$ before reaching 7.552 at $1550^\circ\text{C}$. The value of the parameter $b$ was 7.701 Å at $1250^\circ\text{C}$, value that slightly decreases with
the temperature development up to 7.697 Å at 1550 °C (Tables 3–5). Taking into the account the increase in the alumina content of the mullite crystal with the temperature development, this decrease in the value of parameter b is in agreement with the literature [27]. The parameter c remained constant at 2.890 Å for KY3, KY4 and KY5 for the temperature of 1250 °C and then decreased slightly with temperature development to reach 2.889 Å at 1550 °C. This decrease in volume is correlated with the alumina content (mol%) of a single crystal structure (Fig. 4). The unit parameters a, b, and c as well the crystal volume for the mullite matrix composite confirm the predominance of the mullite 3:2. The data correspond to the space group Pbam. The values of a = 7.54 Å, b = 7.68 Å and c = 2.885 Å are those obtained in Tables 3–5 with some slight differences. These values correspond to x = 0.25 when considering the chemical formula of the mullite. The exact values of the parameters a, b, and c as collected for KY3, KY4 and KY5 agree with those of lattice parameters of mullite containing transition metal cations [27]. In fact if the concentration of Fe2O3 into the matrices under study can be negligible (0.34, 0.29 and 0.26 mass%, respectively, for KY3, KY4 and KY5), the contain of TiO2 are 3.17, 3.21 and 3.24 mass% (Table 1) in the same order and would have modified, with their incorporation into the mullite structure, the lattice parameters. Ti4+ is amongst the cations with the high degree of incorporation into mullite. According to Schneider et al. [27], mullite crystal can incorporated more than 3 mol% of Ti2O3. The 3:2 mullite (x = 0.25), i.e. Al2(Al2.5Si1.5)O9.75, is considered to be the most stable phase amongst others. The 3:2 mullite has highly stable open structure (Tmelt = 1828 ± 10 °C) [28, 29], and it can accommodate a variety of transition metal ions into its structure as a solid solution. Such solid solutions can result in desirable improvements in physical properties such as thermal expansion behaviour, electrical resistivity [30]. The oxidation state of Ti ion favour the anisotropy and its incorporation into mullite structure at the Al3? position in the AlO6 octahedral. The variability in the bond strength along different directions, for example in AlO6 octahedral in mullite, could explain the differences observed in the thermal expansion behaviour. The replacement of Al3+ in the oxygen octahedral with Ti4+ should modify the bonding environment locally and result in different bond strengths and consequently different thermal expansion.

Fig. 8 Micrographs of mullite matrix composites: a KY3, b KY4, and c KY5 at 1550 °C
Mechanical properties

The four-point flexural strength, the Vickers hardness and the elastic modulus of the Kyanite-based mullite matrix composites were used to assess their efficiency to withstand the thermo-mechanical environment which characterizes the refractory matrices.

The variation of the flexural strength of the KY3, KY4 and KY5 with temperature evolution is summarized in Fig. 5. The sample KY3 presents 60 MPa of strength at 1250 °C which is not far from that of the matrix without kyanite [31]. When increasing the kyanite content at the level of 42–50 mass%, the mechanical strength is significantly improved from 60 MPa to >100 MPa for the specimens KY4 and KY5. The role of the particle reinforcement of the fine grains of kyanite is confirmed as they increase in the flexural strength with the increase in the kyanite content and it is linked to the effectiveness of the particles to act as fillers at low temperature and improve the packing process that results in the strength enhancement. The flexural strength of the sample KY3 increased from 60 to 135 MPa when the sintering temperature changed from 1250 to 1350 °C (Fig. 5). Between 1350 and 1550 °C, no more change in strength was observed for the KY3. In contrast, the samples KY4 and KY5 did not present any improvement of strength between 1250 and 1450 °C. The threshold of the flexural strength for both samples is at 1450 °C. The increase in strength between 1450 and 1550 °C is significant for the sample KY5: KY4 has a flexural strength of 150 MPa, while KY5 reached 228 MPa.

The fine particles of Kyanite increase the resistance of the mullite matrix composite to dislocation motion and by the way the hardness. Particles of kyanite can act as dispersion, “solid solution” or grain boundary strengthening mechanisms to provide the strength achieved. They act as pinning impeding dislocation. Since the lattice structure of adjacent grains differs in orientation, it requires more energy for a dislocation to change directions and move into the adjacent grain. The grain boundary is also much more disordered than the inside the grain, which also presents the dislocations from moving in a continuous slip plane. The theory remains the same that more grain boundary, “solid solution” or dispersion create more opposition to dislocation movement and in turn strengthens the material. The action of kyanite is efficient in the ratio where the particles dominate the matrix impeding the destructive action of the residual silica that generally transforms to glassy phase.

Figures 6 and 7 show the Vickers microhardness and the elastic modulus of the samples KY3, KY4 and KY5 at 1550 °C. The Vickers microhardness of KY3 varied from...
7.37 to 16.78 GPa with a mean of 11.54 GPa. That of KY4 is between 7.14 and 28 GPa and from 6.12 to 19.20 GPa for KY5. The elastic modulus varies from 84.3 to 220.2 GPa for KY3 at 1550 °C, 68.4–251.1 GPa for KY4 and from 78.4 to 178.3 GPa for KY5. The mean elastic modulus was 146.2, 129.7 and 109.9 GPa for KY3, KY4 and KY5, respectively. The variation of the bi-axial flexural strength, the Vickers microhardness and the elastic modulus can be interpreted taking into consideration the phenomenon of mullitization and densification in the mullite matrix composites. The continue increase in strength of mullite matrix composite with temperature is primarily explained with the absence or significant reduction in the glassy phase. The introduction of the kyanite particles in the range of the formulations of KY3 gave possibility to metakaolin–bauxite composite to remain the dominant fraction with consequent earlier densification [31]. The earlier densification and the amount of residual silica increase the probability of the glassy phase which in the case of KY3 was enough to increase the elastic modulus while reducing the strength development. KY4 and KY5 correspond to formulations in which the kyanite dominates the matrix and mullite produced from its decomposition is the major phase. It results that the kyanite particles play at low temperature the role of fillers increasing the flexural strength and enhance densification.

At high temperature, they decompose to mullite providing continuity into the matrix. It is well known that the formation of mullite from metakaolin is essentially 3:2 mullite that remains stable up to ~1250 °C. In the presence of kyanite and metastable alumina (calcined bauxite), the crystallization dominate the sintering processes. Kyanite particles play the role of particles reinforcement and phase’s separation between 1250 and 1350 °C, acting as nucleation sites of mullite which in turn affect the microstructure with limited aggregation at low temperature. The absence of liquid phase at this stage reduces the possibility of densification with relative high porosity. The decomposition of the particles reinforcement to mullite at temperature >1350 °C improve the packing process and the cross-linking into the matrix.

**Effects of the kyanite particles into the microstructure of the mullite matrix composites**

The micrographs collected from the specimens of mullite matrix composites up to 1350 °C showed essentially amorphous phase and grains of kyanite. The mullite formed earlier was covered by the high fraction of metastable and amorphous. Mullite grains could be observed in these cases only with etching.
Figures 8 and 9 show the micrographs collected from KY3, KY4 and KY5 at 1550 °C. While it is generally with etching that can be observed mullite grains into the kaolin-based mullite matrix due to the important amount of the amorphous that cover the crystalline grains, we observed grains of mullite in KY3, KY4 and KY5 at 1450 °C just with appropriate polishing. In Fig. 8a, it can be observed the relative difference in morphology of mullite in the context with formation of residual glassy phase although with high viscosity. The micrograph from KY3 at 1550 °C showed optimum densification and larger grain size of mullite with respect to KY4 and KY5 specimens. In general, the kyanite content acts on the size of grains into the microstructure. KY3 exhibited high range of densification, pore reduction and mechanical strength as from 1450 °C due to the dominance in this matrix of the metakaolin–metastable alumina as the major precursor that did not avoid efficiently the liquid phase formation. The pores observed into the micrographs are residual voids that remained with processing and sintering. Temperature development does not have great impact on the microstructure. Unlike KY3, the micrographs of Fig. 8 let observed grains of mullite with very small size without elongation that is generally obtained with the mullite from phyllosilicates [10, 11]. Here, the densification due to the particles reinforcement of kyanite, the absence of glassy phase and amorphous silica did not give possibility to the development of long grains of mullite. Tabular mullite plates with a rounded faces are observed in general for the kyanite-based mullite matrix composites (Figs. 8 and 9). At 1550 °C, KY3 presented optimum densification with the glassy film that appears and responsible of some grains growth at the surface of the matrix. It is at this point that one can really evidence the difference of sintering behaviour and microstructure linked to the content of kyanite. It is observed that in KY3 where metakaolin–metabauxite remain the major solid precursor for the mullitization, some small amount of elongated mullite grains are observed even though this was not enough to affect the final microstructure and the crystal parameters of mullite into the bulk matrix (Tables 3–5; Figs. 8 and 9). The optimum densification in KY3 is evidenced by the mean value of the elastic modulus (150 GPa). This value decreased with the increase in kyanite content, respectively, for KY4 (129 GPa) and KY5 (109 GPa) as it can be observed in Fig. 7. The relative low value of the elastic modulus of KY4 and KY5 is linked to the degree of densification into those matrices. Here, it can be observed that the role of kyanite in delaying the densification is evidenced. It is suggested that the decomposition of the kyanite that happens at high temperature (>1350 °C) reduced the possibility of the development of viscous phase. During the decomposition, some extent of porosity accompanied the crystallization delaying the densification. The absence of viscous phase implies the absence of grain growth. The packing process with very small grains of mullite justifies the high strength and hardness obtained with KY4 and KY5 (Figs. 5–6). Residual alumina grains still to be incorporated into the matrix were identified (Fig. 10), supporting the hypothesis of the reduction in the kinetic of sintering with the composition design and kyanite content. Even though the crystal structure indicated essentially mullite grains type 3:2, from the microstructural analysis; micrographs indicated that the matrices of KY3, KY4 and KY5 contain polycrystalline grains of mullite (Fig. 8). And for the case of KY4 and KY5,
important alumina grains not completely incorporated into the mullite matrix composite (Fig. 10). When kyanite is used as 100 mass% solid precursor for mullite matrix, the microstructure does not show any evidence of grain growth. At the beginning of the transformation of kyanite, and until the final step, needle-like mullite grains are formed directly from kyanite crystals and no change in mullite morphology is observed [12, 13, 32]. The presence of silica coating needle-like mullite grains is the reason proposed [12, 13, 32] to avoid the growth of mullite grains during the decomposition of kyanite.

The use of metastable alumina in this study allow to tackle almost all residual silica as from kyanite and metakaolin to develop additional mullite grains and avoid formation of liquid phase responsible for the expansion of the mullite matrix composite at higher temperature. Avoiding the liquid phase formation maintains the size particles of mullite grains and allows very good packing process and enhances densification with important mechanical properties. In the metakaolin-metastable alumina–kyanite composite under study, the metakaolin ensures the formation of mullite grains at low temperature and by the way provides sufficient strength for the matrix with kyanite acting as particles reinforcement which at this level acts as fillers. At high temperature, the direct transformation of kyanite to mullite ensures an optimum continuity of the matrix with maximum interconnection of mullite grains resulting to a very high compact and strength (Figs. 8–11). The analysis of the porosity and pores size distribution of the matrices KY3, KY4 and KY5 indicated that KY3 fired at 1450 °C was the most porous body (Fig. 12). Increasing the amount of kyanite particles, the size of pores decreased for KY4 and KY5 when consider the same temperature. This is due to the efficiency of the kyanite particles to act as reinforcement closing voids and enhance densification with elimination of the porosity. The relative increase in porosity in KY5 with respect to KY4 at 1450 °C is due to the difference in sintering grade between both matrices at the temperature considered. In general, it was observed that for the range of formulations considered, high amount of kyanite corresponds to some extent at a delay of sintering. The increase in temperature to 1550 °C significantly reduced the pore volume with a shift of the pores bands to high values for the formulation KY3. In fact, the change in pores configuration is attributed the elimination of the interparticles void from the crystallization due to the formation of viscous phase (Fig. 12). This viscous phase is responsible to the formation of a new class of pores evidenced into KY3 and KY5. The particularity of this new class of pores is their size. This type of pores is generally described into ceramic matrix with evidence of sintering including the viscous flow [32, 33]. The absence of this class of pores in KY4 suggests that the formulation is the one that ensures the equilibrium between the mullitization and densification without liquid formation for the design of optimum mullite matrix composite for high temperature applications. In general, the pore network of the mullite kyanite-based mullite matrix composite can be
described in Fig. 13 with the microstructure of the matrix as well as that of the regions of heterogeneity.

Conclusions

The fine particles of kyanite have been successfully used as reinforcements for the production of high strength mullite matrix composites indicated for the applications at high temperatures as refractory components. By applying formulation design, composites including kyanite and metakaolin were developed in which residual silica from both materials is tackled with metastable alumina prepared from bauxite. In the literature, none of metakaolin or kyanite has showed satisfactory results in view of the production of thermally stable matrix composites. It is known that mullite microstructure is different when the raw material is kaolinite from that of kyanite. Kyanite produces tabular mullite plates with rounded faces, different from elongated grains with a large aspect ratio. Mullite matrix composite from kyanite will expand at high temperature, while that from kaolinite will develop microcracks due to the glassy phase formed. A composite of metakaolin and kyanite in which metastable alumina is added results in a mullite matrix composite with improved refractoriness:

1. The amorphous phase content decreased continuously with the temperature up to 1550 °C, the maximum temperature experimented;
2. The absence of glassy phase into the matrix with kyanite >40 mass% permitted to develop densification at very high temperature conducing to very high strength (228 MPa) and hardness (11 GPa);
3. The presence of kyanite particles at low temperature allowed their action as fillers impeding the grain growth of the mullite crystals developed from the metakaolin. In contrast to what is generally observed with the kaolinite–mullite composite [27, 28], no elongated grains were observed in the matrix with kyanite content >40 mass%;
4. At high temperature, kyanite decomposes to mullite maintaining the continuity into the matrix with an improving packing process that induces reduction in porosity and strength enhancement.
5. The high strength and hardness of kyanite-based mullite matrix composite is achieved by its fine microstructure of sub-micrometre grains with reduce grain growth;
6. The mullitization and densification that still ongoing into the matrices with kyanite >40 mass% indicate the suitability of those matrices for high temperature refractory applications.

Since the current trends are oriented to low energy and sustainable processing seeking environmentally friendly products, the kyanite as natural and available raw materials with low global warming potential (GWP) may be interesting option for the design of new mullite matrix composites.

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References

1. Cascales A, Tabares N, Bartolomé JF, Cerpa A, Smirnov A, Moreno R, Nieto MI. Processing and mechanical properties of mullite and mullite–alumina composites reinforced with carbon nanofibers. J Eur Ceram Soc. 2015;35:3613–21.

2. Yang T, Chen J, Li L, Chou KC, Xinmei Hou. Template free synthesis of highly ordered mullite nano whiskers with exceptional photoluminescence. Ceram Int. 2015;41:9560–6.

3. Zake-Tiluga I, Svinka V, Svinka R, Grase L. Thermal shock resistance of porous Al2O3-mullite ceramics. Ceram Int. 2015;41:11504–9.

4. Sousa LL, Souza ADV, Fernandes L, Arantes VL, Salomão R. Development of densification-resistant castable porous structures from in situ mullite. Ceram Int. 2015;41:9443–54.

5. Konegger T, Felzmann R, Achleitner B, Brouczek D. Mullite-based cellular ceramics obtained by a combination of direct foaming and reaction bonding. Ceram Int. 2015;41:8630–6.

6. Almeida MI, Dias AC, Demertzi M, Arroja L. Contribution to the development of product category rules for ceramic bricks. J Clean Prod. 2015;92:206–15.

7. Bribian IZ, Capilla AV, Uson AA. Life cycle assessment of multiwall carbon nanofibers. J Eur Ceram Soc. 2015;35:2427–34.

8. Kashcheev ID, Ust’Yantsev VM, Sychev SN. Kyanite transformation of the Karabash deposit: phase transformations during heating. Refract Ind Ceram. 2007;48(4):250–4.

9. Kashcheev ID, Sychev S, Elizarov A. Effect of oxides RO, R2O3, RO2 and impurity materials on decomposition during heating of kyanite in oxidizing and reducing atmospheres. Refract Ind Ceram. 2011;52(1):44–7.

10. Boussois K, Deniel S, Tessier-Doyen N, Chatteigner D, Dublanchixier C, Blanchart P. Characterization of textured ceramics containing mullite from phyllosilicates. Ceram Int. 2013;39:5327–33.

11. Deniel S, Tessier-Doyen N, Dublanchixier C, Chatteigner D, Blanchart P. Processing and characterization of textured mullite ceramics from phyllosilicates. J Eur Ceram Soc. 2010;30:2427–34.

12. Sainz MA, Serrano FJ, Bastida J, Caballero A. Microstructural evolution and growth of crystallite size of mullite during thermal transformation of kyanite. J Eur Ceram Soc. 1997;17:1277–84.

13. Rahbar N, Aduda BO, Zimba J, Obwoya SK, Nyongesa FW, Yakub I, Soboyejo WO. Thermal shock resistance of a kyanite-based (aluminosilicate) ceramic. Exp Mech. 2011;51(2):133–41.

14. Njoua A, Nkoumbou C, Grosbois C, Njoupwo D, Njoua D, Courtin-Nomade A, Yvon J, Martin F. Genesis of Mayoumou kaolin deposit (western Cameroon). App Clay Sci. 2006;32(1–2):125–40.

15. Tchamba AB, Melo UC, Kamseu E, Yongue R, Njoupwo D. Thermal and sintering behaviour of bauxite from Hallo-Danielle Mimim-Matap (Cameroon). Ind Ceram. 2010;3:1–6.

16. Larson AC, Von Dreele RB. GSAS: Generalized structure analysis system. 1994, Laur 86–748. Los Alamos: Los Alamos National Laboratory.

17. Tobin BH. EXPGUI, a graphical user interface for GSAS. J Appl Crystallogr. 2001;34:210–3.

18. Gualtieri AF. Accuracy of XRPD QPA using the combined Rietveld-RIR method. J Appl Crystallogr. 2000;33:267–78.

19. Bernasconi A, Dapiglia M, Gualtieri AF. Accuracy in quantitative phase analysis of mixtures with large amorphous contents. The case of zircon-rich sanitary-ware glazes. J Appl Crystallogr. 2014;47:136–45.

20. McCusker LB, Von Dreele RB, Cox DE, Louër D, Scardi P Rietveld refinement guidelines. J Appl Crystallogr. 1999;32:36–50.

21. Kim J, Kim DI, Zi G. Improvement of the biaxial flexure test method for concrete. Cem Conc Compos. 2013;37:154–60.

22. Kirane K, Bazant ZP, Zi G. Fracture and size effect on strength of plain concrete disks under biaxial flexure analyzed by microplane model M7. J Eng Mech. 2014;140:604–13.

23. Marshal DB, Tatsuoo N, Evans AG. Simple method for determining elastic modulus to hardness ratios using Knoop Indentation Measurements. J Am Ceram Soc. 1982;65:C-175.

24. Brindley GW, Nakahira M. The kaolinite–mullite reaction series: I. A survey of outstanding problems. J Am Ceram Soc. 1959;42:311–4.

25. Brindley GW, Nakahira M. The kaolinite–mullite reaction series: II Metakaolin. J Am Ceram Soc. 1959;42:315–8.

26. Brindley GW, Nakahira M. The kaolinite–mullite reaction series: III. The high temperature phases. J Am Ceram Soc. 1959;42:319–24.

27. Schneider H, Schreuer J, Hildman B. Structure and properties of mullite—a review. J Eur Ceram Soc. 2008;28:329–44.

28. Saalfeld H, Guse W. Structure refinement of 3:2 mullite (3Al2O3.2 SiO2). N Jb Miner Mh. 1981;14:145–50.

29. Rahman S, Freimann S. The real structure of mullite. In: Schneider H, Komarneni S, editors. mullite. Weinheim: Wiley; 2005. p. 46–70.

30. Schmucker M, Mackenzie KJD, Smith ME, Caroll DE, Schneider H. AlO4/SiO4 distribution in tetrahedral double chains of mullite. J Am Ceram Soc. 2005;88:2935–7.

31. Jangang CN, Tchamba AB, Kamseu E, Melo UC, Elimi B, Ferrari AM, Leonelli C. Reaction sintering and microstructural evolution in metakaolin-metastable alumina composites. J Therm Anal Calorim. 2014;117(3):1035–45.

32. Dutou NJG, Mohamed H, Nzeukou NA, Kamseu E, Melo UC, Beda T, Leonelli C. The role of kyanite in the improvement in the crystallization and densification of the high strength mullite matrix: phase evolution and sintering behaviour. J Therm Anal Calorim. 2016;126(3):1211–22.

33. Ban T, Okada K. Structure refinement of mullite by the Rietveld method and a new method for estimation of chemical composition. J Am Ceram Soc. 1992;75:227–30.