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Stabilized tialite–mullite composites with low thermal expansion and high strength for catalytic converters

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Abstract

Aluminium titanate (AT) is a potential candidate material for use in demanding high temperature applications, because it exhibits an excellent thermal shock resistance due to its low thermal expansion coefficient and high refractoriness.

However, industrial applications of this material are hindered by two major limitations. Its decomposition to α-Al_2O_3 and TiO_2 between 800 and 1280 °C and its low mechanical strength.

The present work aims to stabilize aluminium titanate with the addition of Fe_2O_3. The decomposition of aluminium titanate–iron oxide solid solutions when heated at 1100 °C for up to 1000 h was studied. The effect of iron oxide addition on pure aluminium titanate properties was investigated. Additionally, strengthening of the iron stabilized AT with mullite was considered adding mullite (M), $3Al_2O_3{\cdot}2SiO_2$ to tialite body at various amounts (5–50%, w/w). Properties like four point bending strength, thermal expansion coefficient (TEC), and porosity of the composites, were evaluated. Finally, the effect of mullite on the mechanical properties of AT–mullite composites was investigated.

It was found that aluminium titanate (iron oxide stabilized)–mullite composites exhibit very good mechanical strength combined with excellent thermal stability.

Keywords: Thermal expansion; Mechanical properties; Al_2TiO_5; Mullite; Chemical stability

1. Introduction

Aluminium titanate, Al_2TiO_5 (AT) is a ceramic material formed by a solid state reaction of equimolar mixtures of Al_2O_3 and TiO_2 carried out in the range 1360–1400 °C and it remains stable up to its melting point (1860 °C).[1,2]

Aluminium titanate based ceramics exhibit a series of outstanding properties which make them suitable for a wide range of modern applications particularly in the automotive industry. Tialite is known, as a candidate material for use at demanding high temperature applications, because it is an excellent thermal shock resistant material, it has very low thermal expansion coefficient ($10^{-6}\,°C^{-1}$) and low thermal conductivity ($0.9–1.5\,W\,m^{-1}\,°C^{-1}$). It is also used for the construction of internal combustion engines, in metallurgical applications as well as for thermal barriers.[3–5]

However, industrial applications of this material are hindered due to two major limitations. The first one concerns with its tendency to decompose to α-Al_2O_3 (corundum) and TiO_2 (rutile) at temperatures between 800 and 1280 °C.[6,7] The second is due to its very low fractural strength owing to the development of extensive microcraking during cooling from sintering to room temperature.[8]

The structure of AT is isomorphous with mineral pseudobrookite ($M_2{}^{3+}Ti^{4+}O^5$) structure crystallizing in the orthorhombic space group. In this structure each Al^{3+} or Ti^{4+} cation is surrounded by six oxygen ions forming distorted oxygen octahedra. These octahedra form chains weakly bonded to each other. This structure results to the strong thermal anisotropy which creates a complicated system of localized internal stresses during cooling, causing extensive microcracking that is responsible for the mechanical weakness of the material and also for its low thermal expansion. On the other hand, microcracks contribute to a low thermal conductivity to and an excellent thermal shock resistance.[9,10]

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Experimental evidence about the decomposition phenomenon, suggests a nucleation and grain growth controlled process, affected by the characteristics of the initial powder and the processing variables (compaction pressure, sintering temperature and time).[11,12] The degradation of tialite is mostly related to the thermodynamic instability of AT. The maximum decomposition rate is reached between 1100 and 1150 °C and the reaction completes after 5–50 h.[13] Yet, the decomposition temperature is believed to change depending on precursor's particle size.[12–14] Some oxide dopants like SiO_2, ZrO_2,[11] MgO,[10,14,15] Fe_2O_3,[2,16] mullite,[17–20] $ZrSiO_4$[14] and rare-earth oxides have been used to control the decomposition. Among these stabilizers, Fe_2O_3 and MgO appear to offer a high degree of phase stability in critical conditions. Even though, decomposition and stabilization mechanisms are not yet clearly understood, however, it is obvious that microstructure is strongly affected by the amount and the nature of the stabilizing additive.

Most pseudobrookite structures are characterized by unusually high expansion coefficients (TEC) along the principal crystallographic directions. (Tialite: $\alpha_a = -3 \times 10^{-6}\,{}^{\circ}C^{-1}$, $\alpha_b = +11.8 \times 10^{-6}\,{}^{\circ}C^{-1}$, $\alpha_c = 21.8 \times 10^{-6}\,{}^{\circ}C^{-1}$.) Correlating grain size and microcracks formation it is referred that although microcraking phenomenon appears at a grain size as low as 0.5–1 μm,[21,22] an average grain size of 3–4 μm is necessary for the microcracks to have any significant effect on the properties of the ceramic.[23,24] The mechanical strength can be significantly improved by the addition of a material of high strength, to form a microstructure, in which the tialite grains are surrounded by the grains of the high strength component. A combination between the properties of the host and the dopant material offers the opportunity to tailor the required properties through the selection of composite compositions.

Additives like ZrO_2,[8,25] $ZrTiO_4$,[25,26] $3Al_2O_3{\cdot}2SiO_2$,[19] $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ have been proposed. Mullite, $3Al_2O_3{\cdot}2SiO_2$ (M) is a strong material with moderate thermal expansion behavior ($\alpha_{25-1500\,{}^{\circ}C} = 6.9 \times 10^{-6}\,{}^{\circ}C^{-1}$) so it seems to be a potential additive.[27]

The aim of this work, which is the part of an extensive research project, is the production of a tialite based material with improved thermal stability and mechanical strength suitable for high temperature applications such as automotive catalytic converters. The composite material has to fulfill the following requirements: (i) thermal stability, (ii) low TEC values ($\approx 0 \times 10^{-6}\,{}^{\circ}C^{-1}$), (iii) high porosity (≥30%) and (iv) high mechanical strength (≥18 MPa).

The first objective of this work, was the stabilization of AT by iron additions. A study was carried out on the thermal stability of $Al_{2(1-x)}Fe_{2x}TiO_5$ solid solutions ($0 \leq x \leq 20$), when heated for 100–1000 h at 1100 °C. Furthermore, the effect of various iron oxide amounts on stabilized aluminium titanate properties (strength, porosity, thermal expansion), was investigated.

Subsequently, strengthening of the optimum stabilized AT, was attempted via mullite (M), $3Al_2O_3{\cdot}2SiO_2$ additions (5–50%, w/w). Microstructural, thermal and mechanical properties of the composite material produced, were studied and evaluated. In both cases (stabilization and strengthening), the influence of sintering temperature on the properties was evaluated.

2. Experimental procedure

2.1. Preparation of the powders

Aluminium titanate was synthesized by reaction sintering of stoichiometric amounts of corundum Al_2O_3 (Nabalox), rutile TiO_2 (Unitec) and iron oxide Fe_2O_3 (Aldrich, 99% purity). Appropriate amounts of reactants were used in order to prepare Al_2TiO_5 containing 5–20 mol% Fe_2O_3. The powders were mixed by wet-milling using water and alumina balls for 24 h. The resulting powders after drying were heated at 1400 °C for 3 h. The phases present were identified by an X-ray diffractometer (XRD, Siemens, D-500). Ten weight percent Si (Alfa) was added to the powders before the measurement as internal standard. Mixtures of tialite (Fe_2O_3 stabilized) with mullite (5, 10, 15, 20, 30, 50, w/w) were wet-milled for 3 days and subsequently dried.

2.2. Extrusion as rods

The powders were mixed with cellulose (MHPC 20000), sodium stearate and distilled water. The mass produced, was extruded as rods. The samples were dried and sintered at 1350, 1400, 1450, 1500 and 1550 °C for 3 h. Ageing experiments included thermal treatment at 1100 °C for 100, 300, 600 and 1000 h.

2.3. Evaluation–characterization

The samples were characterized in terms of: (i) flexural strength by four point bending strength tests (INSTRON 8562), (ii) thermal expansion behavior (dilatometry DIL 402, Netzch), (iii) porosity calculated by Archimedes method and (iv) microstructure by SEM (Jeol-6300).

3. Results and discussion

3.1. Stabilization of aluminium titanate

3.1.1. Phase composition

Fig. 1 presents XRD patterns of AT stabilized with Fe_2O_3 after its exposure to 1100 °C for 1000 h. As it is observed, tialite stabilized with 5 mol% Fe_2O_3 is completely decomposed after 1000 h. Even when the amount of the iron used was increased to 10 mol%, thermal degradation of tialite remained high. Two sharp peaks of rutile and corundum, appear on both sides of the main AT peak which is almost vanished (Fig. 1).

Similarly, when the quantity of the stabilizing agent was increased to 15 mol% the level of the decomposition was obviously lowered, but still not vanished. The addition of 20 mol% iron oxide was necessary to suppress the thermal decomposition of tialite. The material survived throughout the ageing tests (Fig. 2) as tialite remained practically unaltered. Although in Figs. 1 and 2 there is a small amount of decomposition products

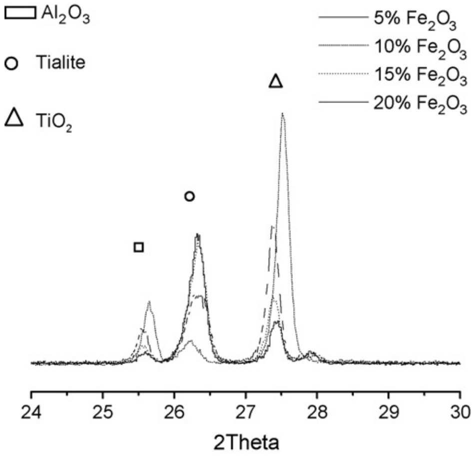

Fig. 1. XRD patterns of AT–x mol% Fe_2O_3 (x = 5, 10, 15, 20%) after 1000 h at 1100 °C.

it is however obvious that the material is very stable at 1100 °C. The stabilizing effect of the agent used is profound and it is important to explain why iron influences, rather strongly, the decomposition process.

According to previous works[2,28] decomposition occurs because lattice site occupied by aluminium (Al^{3+} ionic radius = 0.053 nm) is too large. The available thermal energy permits aluminium to migrate from its site resulting to a structural dissolution to rutile and corundum. On the contrary, iron cations (Fe^{3+} ionic radius = 0.064 nm) fit in very well thus reducing the decomposition reaction rate to a minimum. The presence of Fe_2O_3 in the system results in decreasing the reaction temperature for the formation of AT while the rate of AT formation is increased. Thus, the addition of Fe_2O_3 has a catalytic effect on the kinetics of the AT forming reaction.[2]

Partial substitution of Al^{3+} ions by Fe^{3+} ions in Al_2TiO_5 leads after total reaction to the formation of solid solutions with the general formula $Al_{(1-x)2}Fe_{2x}TiO_5$ after completion of the reaction. Indeed Fig. 3 presents X-ray spectra of aluminium titanate stabilized with 5–20 mol% Fe_2O_3. Silicon is used as internal standard. As it can be seen, XRD patterns of stabilized tialite are similar to the pure tialite but with some angular shift. Tialite's main peak moved to smaller angles as the amount of iron in AT body is increased. This is attributed to the substitution mentioned before, which results in an enlarged unit cell with increased lattice dimensions. Iron atoms which are dispersed throughout AT matrix, enter into the unit cell to form pseudobrookite structures (Fe_2TiO_5) in solid solution with Al_2TiO_5. Thus, even though the stabilized percentage is quite high (20 mol%), there is not any peak corresponding to iron compounds.

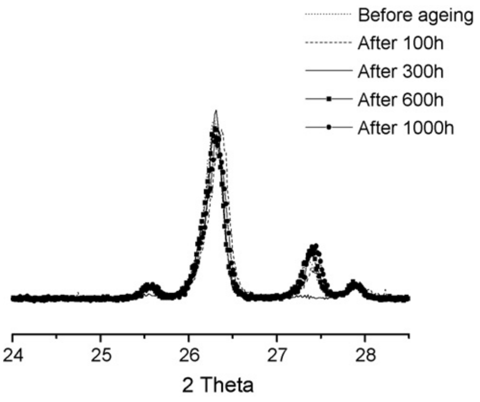

Fig. 2. XRDs of AT–20 mol% Fe_2O_3 after 100, 300, 600 and 1000 h at 1100 °C.

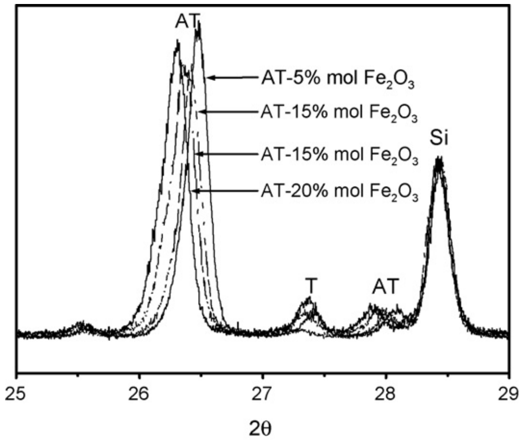

Fig. 3. XRD patterns for iron stabilized tialite (AT: aluminium titanate; T: titanium oxide; Si: silicon).

Consequently, it is believed that the improvement of tialite's chemical stability is affected by two major factors: (a) the formation of a solid solution between the tialite phase and iron oxide (thermodynamic effect), and (b) the partial but strong suppress of decomposition reaction of the Al_2TiO_5–Fe_2TiO_5 solid solution (kinetic effect).[29]

3.1.2. *Mechanical strength*

The admittedly weak tialite's structure is improved by the addition of iron oxide (Fig. 4). Flexural strength of the samples sintered at 1450 °C is increased from 8.472 MPa for AT–5 mol% iron oxide, to 17.21 MPa for AT–20 mol% iron oxide. This may be attributed to the presence of iron that decreases the required sintering temperature.

3.1.3. *Thermal expansion*

Thermal expansion coefficient (TEC) of stabilized tialite, takes lower values comparing to pure material (Fig. 5). The

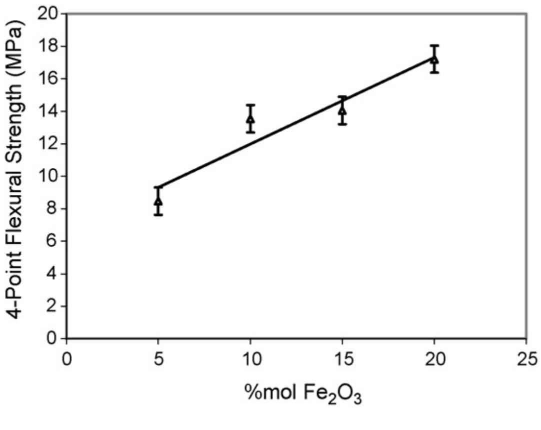

Fig. 4. Flexural strength of AT vs. mol Fe_2O_3 and sintered at 1450 °C.

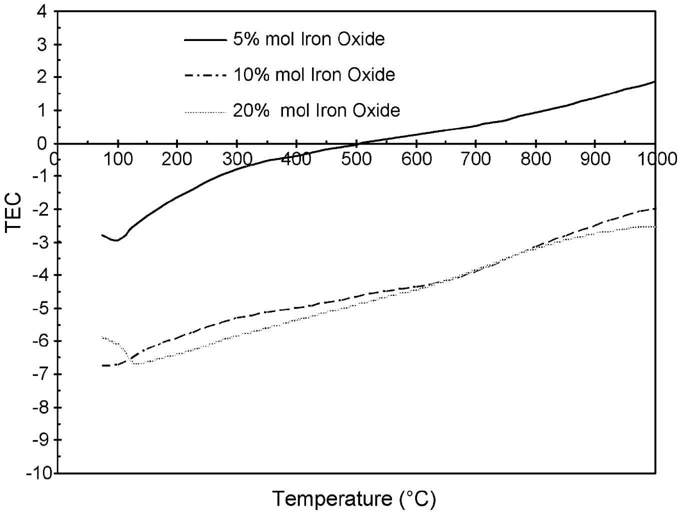

Fig. 5. Thermal expansion coefficient ($\times 10^{-6}\,^{\circ}C^{-1}$) of Al_2TiO_5 stabilized with iron oxide.

general trend appears to be a gradual drop in bulk thermal expansion as iron content increases. Fig. 5 presents thermal expansion curves of low (AT–5 mol% Fe) and high iron doped (AT–20 mol% Fe) materials. The thermal expansion curve of the first one is very close to zero while the second one is shifted to negative values. The existence of extensive microcracking provides the space necessary to accommodate the particle's thermal motion without thermal expansion.

Taking into consideration all the experimental results, it is suggested that the optimum quantity of iron is 20 mol%. The material produced is chemically stable at tough conditions prevailing during the operation process in a car engine. The temperature prevailing in car catalyst is around 600 °C and temporary reaches at 1000 or 1100 °C. This means, that a life time of at least 1000 h at 1100 °C without decomposition, is very sufficient.

3.2. Addition of mullite

After achieving the first goal that is chemical stability the interest is focused to improve the flexural strength of stabilized tialite while at the same time to ensure that its TEC values are kept near zero. Tialite used in the following tests, has been stabilized with 20 mol% Fe_2O_3, and therefore the abbreviation AT20Fe will be used throughout the text for convenience.

Mullite was used in the present work as an additive with the objective to improve flexural strength of AT20Fe. It was selected because it has a positive thermal expansion coefficient ($TEC \approx 5 \times 10^{-6}\,^{\circ}C^{-1}$), high flexural strength and high melting point.[30] Combination between the properties of AT20Fe and the mullite offers the opportunity to tailor the properties of the final composite material.

Furthermore, the effect of mullite addition on tialite's thermal stability was expected to be positive according to the available literature. It has been reported by Tsetsekou[19] and Low et al.[28] that the presence of 20 wt.% mullite is also effective in stabilizing AT against thermal decomposition. Although structure stabilization in AT has been poorly understood it is probable that the presence of an additive may help to limit the level of internal stresses caused by the anisotropic thermal expansion of the individual grains.[30]

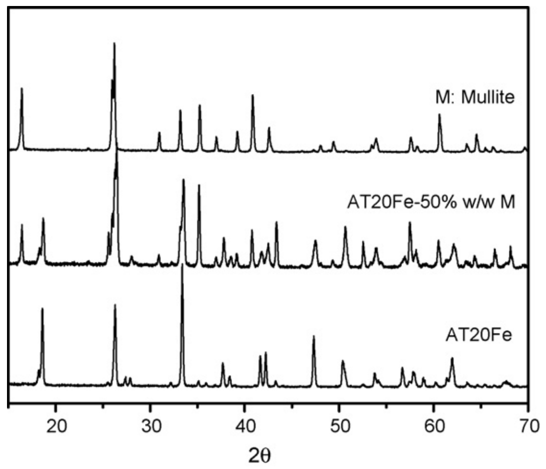

Fig. 6. XRD patterns for AT20Fe, mullite (M) and AT20Fe–50% M.

3.2.1. Phase composition

Fig. 6. presents the XRD patterns of AT20Fe, pure mullite and AT20Fe doped with 50% (w/w) mullite. It is observed that the diffractogram of the composite material appears as the sum of the single diagrams for Al_2TiO_5 and mullite. This observation suggests that no reaction between AT20Fe and mullite has taken place. Mullite grains just enter into the matrix and settle between the AT20Fe grains forming the composite material. A more detailed discussion about this phenomenon is carried out below.

3.2.2. Mechanical strength

Composite tialite based materials exhibited a wide range of mechanical strength values at four point bending tests. The results showed that there is a strong correlation of the mechanical strength to the quantity of the mullite added as well as of the sintering temperature used (Fig. 7). As mullite addition

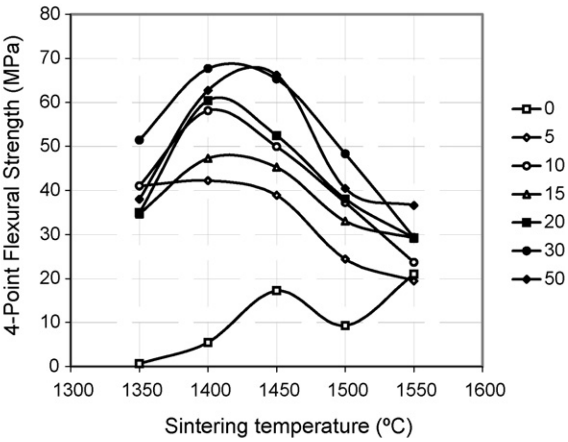

Fig. 7. Flexural strength vs. temperature for tialite (20 mol% iron oxide stabilized)–mullite composites.

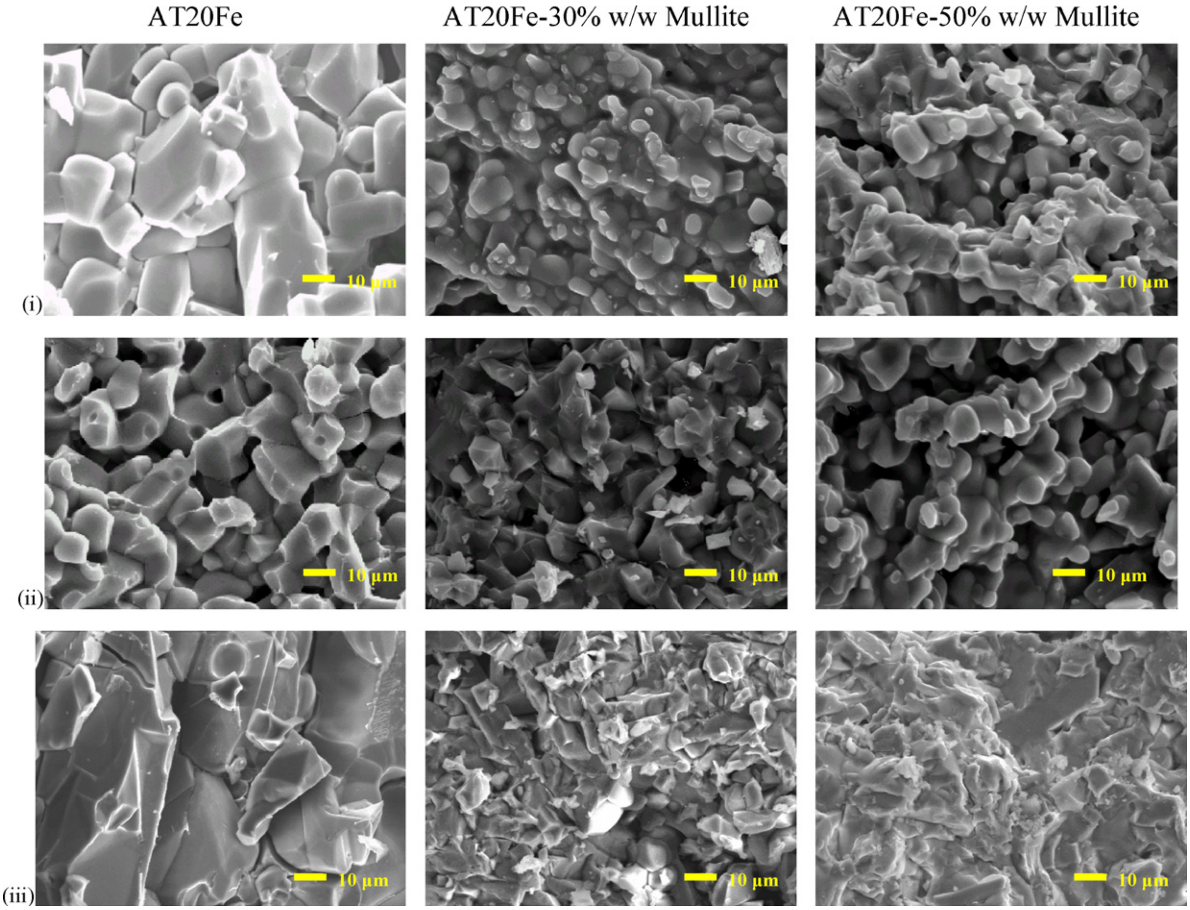

Fig. 8. SEM images (×2500) for AT20Fe–mullite composites sintered at: (i) 1400 °C, (ii) 1450 °C and (iii) 1550 °C.

increases from 0 to 30% the flexural strength increases from 5.5 to 67.7 MPa.

The strengthening mechanism involves the entrance of mullite into the matrix and its dispersion along tialite's grain boundaries. Mullite, except for being a strong material, acts also as a crack stopper minimizing the problem of crack propagation.[30] Besides it has a pronounced effect on the microstructure of the material. Scanning electron micrographs of AT–mullite composites (Fig. 8) revealed some apparent changes on the structure, concerning the grain size. In Fig. 8(i–iii) the effect of mullite content and the firing temperature on the composite's microstructure are shown. It is evident that as mullite content increases the grains tend to be finer while microcracks are decreasing not only in number but also in intensity. For 50% (w/w) mullite content detrimental microcracks are almost vanished for all sintering temperatures On the other hand increasing of the firing temperature results in coarsening of the grain size. This is particularly true for samples fired at 1550 °C. Microcracks of a higher number and intensity are observed as the firing temperature increases causing a decrease in the mechanical strength.

In Table 1, the values of mechanical strength and porosity are tabulated for composites with an increasing percentage of mullite, sintered at 1350, 1400, 1450, 1500, 1550 °C. For the

Table 1
Flexural strength–porosity for AT20Fe–mullite composites

Mullite (%, w/w)	1350 °C	1400 °C]		1450 °C		1500 °C		1550 °C		P (%)
	σ (MPa)	P (%)	σ (MPa)	P (%)	σ (MPa)	P (%)	σ (MPa)	P (%)	σ (MPa)	
0	0.7(±0.3)	33	5.5(±0.7)	25	17.2(±0.8)	24	9.2(±0.7)	14	21.0(±1.0)	16
5	41.0(±2.0)	24	42.2(±0.7)	15	38.9(±0.7)	11	24.9(±1.2)	12	19.4(±2.5)	16
10	41.0(±1.5)	25	58.1(±2.0)	14	49.9(±2.2)	11	37.2(±1.0)	11	23.7(±0.7)	15
15	34.6 (±1.9)	28	47.3(±1.1)	15	45.3(±1.3)	10	33.0(±1.1)	10	29.2(±0.9)	15
20	34.9(±1.2)	29	60.4(±2.5)	16	52.5(±3.0)	11	38.1(±1.3)	10	29.2(±0.4)	15
30	51.5(±2.0)	27	67.7(±0.9)	14	65.3(±1.4)	11	48.3(±2.4)	11	29.3(±1.4)	12
50	38.0(±1.3)	37	62.7(±3.0)	15	66.2(±0.9)	11	40.5(±0.3)	9	36.6(±1.0)	12
50 + 20% organic	17.6(±0.3)	50	28.3(±1.3)	41	36.9(±1.3)	37	30.4(±0.8)	26	28.3(±3.0)	19

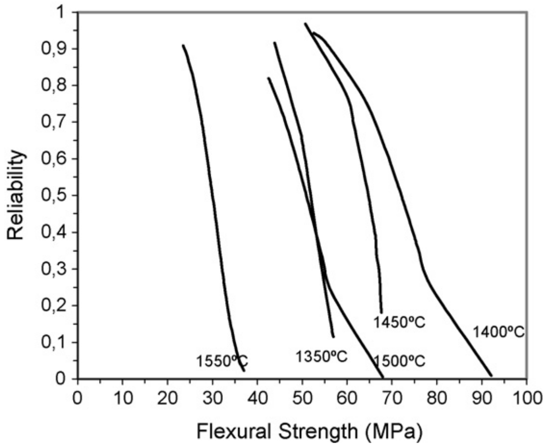

Fig. 9. Flexural strength reliability for tialite (20 mol% iron oxide stabilized)–30% (w/w) mullite composite.

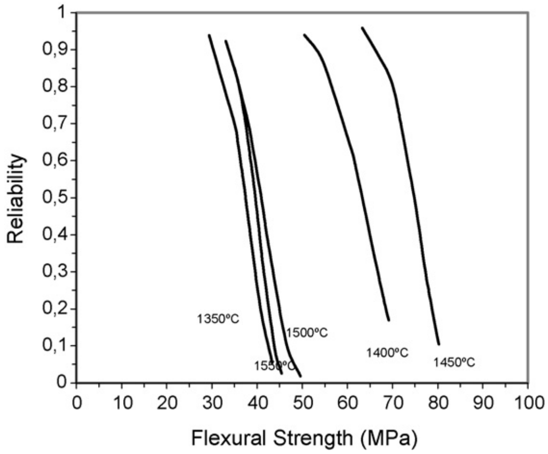

Fig. 10. Flexural strength reliability for tialite (20 mol% iron oxide stabilized)–50% (w/w) mullite composite.

same mullite percentage the mechanical strength is maximum for the samples sintered at the temperature range 1400–1450 °C. Sintering at 1450 °C results in reduced porosity combined with a slight decrease of the mechanical strength. Sintering at 1550 °C results in a profound decrease of the mechanical strength combined with an increase in the porosity. Clearly for a sintering temperature over 1450 °C the material becomes more brittle possibly due to the melting initiation as a result of Fe_2O_3 doping. This phenomenon is more pronounced at sintering temperature of 1550 °C where over firing results in bloating and mechanical strength decrease.

Although the mechanical strength of the composite materials sintered at 1400–1450 °C is very satisfactory, there is still a demand for a more porous material for the application in concern. Porosity proved that it can be easily increased by the use of an organic pore forming agent or by lowering the sintering temperature. When a porosity agent was added (e.g. 20%, w/w) the porosity of AT20Fe–50% (w/w) mullite composite, increased from 15 to 41% (at 1400 °C). Many of the composite materials investigated could be suitable as substrates in catalytic converters based on their mechanical properties.

However, anisotropic materials have different mechanical properties in different directions and as a consequence they present varying strengths. This leads to the necessity of employing statistical analysis for their utilisation in design and manufacturing. The variation of fracture strength of stabilized tialite doped with mullite has been modeled using Weibull distribution analysis.[31–33] Using the previous test data, the corresponding Weibull distribution was determined. Figs. 9 and 10 illustrate the reliability versus strength diagram of AT20Fe–30% and 50% (w/w) mullite composites, of samples sintered at 1350, 1400, 1450, 1500 and 1550 °C. Weibull plot, allows the prediction of the stress, at which the probability of survival is kept to a certain value.

Both diagrams show that tialite–mullite composite ceramics offer high reliability of survival (higher than 90%), even at extremely high stress values. In the first case (30%, w/w, mullite), the reliability of survival at 45 MPa is over 90% for all sintering temperatures except 1550 °C. In the second (50% mullite) the same reliability is evident for stress of 45 MPa at sintering temperature 1400–1450 °C. In other words choosing an amount of the mullite addition between 30 and 50% and the sintering temperature it is possible to prepare ceramics with desirable mechanical strength characterized by high reliability.

3.2.3. Thermal expansion

Thermal expansion curves of tialite–mullite materials demonstrated a deep influence of second phase's expanding behavior, on tialite's contracting behavior. Higher quantity of mullite results to higher TEC values. Fig. 11 represents thermal expansion behavior of tialite–mullite composites sintered at 1400 °C. The curve of pure tialite is below zero ($\mathrm{TEC}_{\mathrm{AT20Fe}}^{600\,^{\circ}\mathrm{C}} \approx -5 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$), but is gradually shifting up as mullite additions increase. It should be pointed out, that the composition with 30% (w/w) mullite, has an almost zero thermal expansion behavior.

The addition of the second phase (mullite) is very effective for suppressing grain growth and gives a fine grained structure while at the same time it increases the apparent thermal expansion of the polycrystalline material.[34,35].

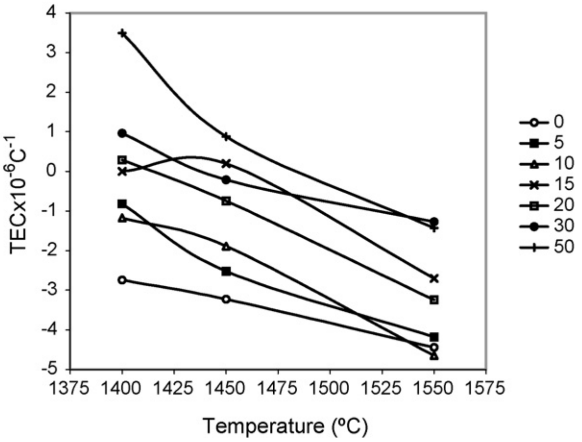

Fig. 11. Thermal expansion coefficient values for AT20Fe–mullite composites vs. sintering temperature.

4. Conclusions

1. Iron oxide added in tialite creates a solid solution and acts as a stabilizer. Although the stabilizing effect is evident even for low iron oxide additions, a 20 mol% addition is necessary for full stabilization.
2. Iron oxide acts not only as a stabilizer but it has a pronounced effect on the properties of tialite. Increasing amounts of iron oxide result in:
   - Increasing of the mechanical strength.
   - Decreasing of thermal expansion.
   - Decreasing of refractoriness.
3. Mullite addition was found to be very beneficial on the properties of the composite stabilized tialite–mullite. Increasing amounts of mullite result in:
   - Increasing of TEC. For 30–50% (w/w) mullite TEC values at 600 °C were close to zero. The positive TEC of mullite compensates for the negative TEC of aluminium titanate (fully stabilized with iron oxide). Thus, the composite structure has a TEC of nearly zero.
   - Increasing of mechanical strength. Mullite acts as a crack stopper thus arresting the propagation of tialite's microcracks.
4. Based on the results of sintering experiments the optimum temperature range for sintering of tialite (iron stabilized)–mullite composites is 1400–1450 °C.
5. Tialite (iron stabilized)–mullite composites are very suitable for the construction of ceramic substrates for automobile catalysts because:
   - They present high structural stability.
   - They are characterized by near zero TEC coefficients.
   - Their flexural strength is high (>62 MPa).

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