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Anisotropic behaviour of andalusite particles used as aggregates on refractory castables

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Abstract

Andalusite is a well known alumino-silicate mineral largely employed in the refractory industry in order to provide high mechanical properties and thermal shock resistance. This work is devoted to the study of the thermal expansion behaviour of andalusite aggregates used in refractory castables. Anisotropic thermal expansion behaviour has been underlined by dilatometric measurements on andalusite single crystals according to their crystallographic axes. This behaviour can be magnified by the presence of quartz, even in small quantity, as impurities in the andalusite particle. The anisotropy of dilation is preserved after mullitisation of andalusite. These important results make it possible to explain the origin of the diffuse damage observed in andalusite-based castables which is most probably responsible for the enhancement of the strain to rupture required for the good thermal shock performance of such material.

Keywords: Andalusite; Anisotropy; Thermal expansion; Thermal shock resistance; Mechanical properties; Refractories

1. Introduction

Refractories play an essential role in a wide variety of high temperature applications and are used in many strategic industries such as the making of steel, cement or glass. Over the past 15 years, the steel-making industry has consolidated its production system by several means (mergers, grouping and personnel retrenchments). This market for refractories has encouraged the producers to improve the durability, the reliability and the workability of such materials. Although refractories have been continuously developed, with notable improvements in their chemical, thermo-mechanical and functional properties, thermal shock remains one of the main causes of early failure in steel or iron mass production installations. In fact, the design and the development of refractories with tailored thermal shock behaviour requires a good understanding of the structural properties of the materials from the micro-scale (sometimes even from nano-scale) to the macro-scale. In particular, the knowledge of phenomena acting at the interface between aggregates and matrix (fine particles including cement) is essential to better apprehend the mechanical behaviour of castables. Of course, all these investigations have to be performed according to the temperature considering the associated phase transformation processes.

In the case of refractory castables, these materials generally present complex heterogeneous microstructures which can induce, according to temperature variation, thermal expansion mismatch between constituents and strong internal stresses. Depending on the thermal history, this internal stress field can modify the microstructural state of the material and thus can also strongly affect its thermo-mechanical behaviour[1,2]. As presented in several recent works[3–6] dealing with the thermo-mechanical behaviour of such materials, the nature and specifically the properties (thermal, mechanical) of the components can play a crucial role on the development of a diffuse microcracking network induced by thermal expansion mismatch between the matrix and the aggregates. This microcracking network leads to the occurrence of a distinctly non-linear mechanical behaviour which is more suitable in case of thermal shock applications (Fig. 1).

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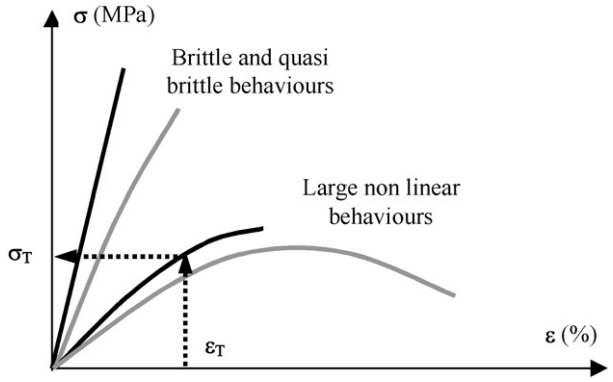


Fig. 1. Typical stress–strain behaviours observed on refractory materials and consequence on stress level involved by a given thermal shock in using conditions.

The aim of the work reported here is to present experimental results focused on the thermal expansion behaviour of a specific aggregate, andalusite, which is commonly used to design refractory castables. Here, the availability of large size andalusite single crystals makes it possible to emphasise the anisotropy of the dilatometric behaviour (according to measurements carried out along the different crystallographic axes) of these aggregates, in their initial state and after mullitisation.

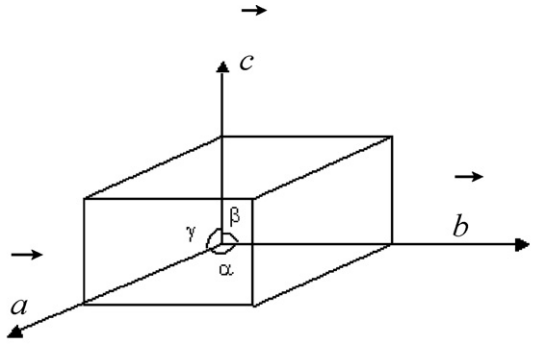
2. Materials and experimental methods

2.1. Materials

2.1.1. Literature on andalusite crystal

Andalusite (Al_2O_3, SiO_2) is a member of the aluminosilicate minerals. The crystalline structure[7] of andalusite is orthorhombic type ($\vec{a} \neq \vec{b} \neq \vec{c}$, $\alpha = \beta = \gamma = 90°$), with the unit-cell parameters indicated in Fig. 2.

Because of the excellent high temperature volume stability, mechanical strength, thermal shock resistance and creep resistance of andalusite, refractories with such aggregates have been used in many industrial fields, such as the metallurgical industry and building materials industry[8,9]. Due to the morphology of andalusite grains in their gangue (Fig. 3), andalusite aggregates, used in refractory materials, are typically made of a single crystal or of a fragment of single crystal. The andalusite content in conventional raw materials usually ranges around 90–95% by weight and the main mineral impurities are typically quartz, biotite, ilmenite and pyrite[10]. Usually, these impurities are concentrated in a characteristic (Fig. 3) cross-located right in the centre of the andalusite single crystal section. This specific cross-pattern can evolve to a square geometry along the *c* axis of the single crystal.



	$\vec{a}$	$\vec{b}$	$\vec{c}$
Unit-cell values	7.76 Å	7.92 Å	5.57 Å

Fig. 2. Unit-cell parameters of andalusite (orthorhombic structure).

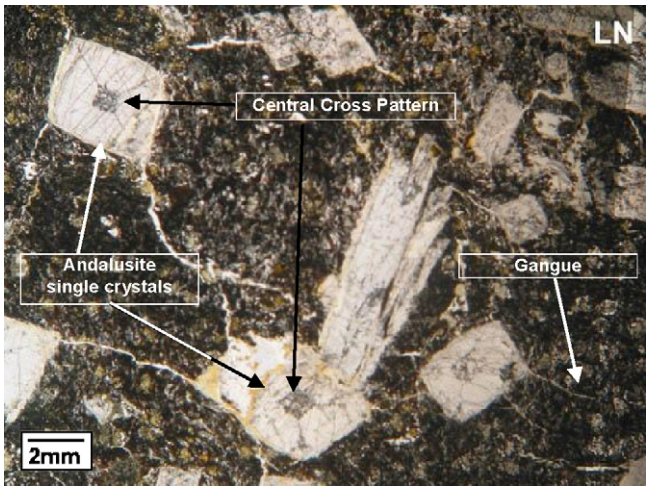


Fig. 3. Optical microscopy of andalusite crystals in their gangue.

During heating, andalusite single crystals are progressively transformed, above 1280 °C, into a composite made of mullite ($3Al_2O_3$, $2SiO_2$) with a capillary network filled with silica (SiO_2). Mullite is topotactically oriented in relation with the host crystal with its *c* axis parallel to the *c* axis of the initial andalusite[11–13]. Until today, very few works have been devoted to the study of the thermal expansion behaviour of this aggregate in its initial and/or mullitised form.

The most remarkable one, a study concerning the thermal expansion behaviour of Al_2SiO_5 polymorphs (andalusite, kyanite, and sillimanite) carried out at a very small scale, was performed by Winter and Ghose[14]. The authors, using the powder-diffraction technique, have measured the evolution of the unit-cell parameters of pure andalusite crystals in the 20–1000 °C temperature range (Fig. 4). From these measurements, a strong anisotropy of the coefficient of thermal expansion (CTE) "d(unit-cell dimension)/d*T*" appears between the different axes of the orthorhombic unit-cell: $d\vec{a}/dT > d\vec{b}/dT > d\vec{c}/dT$. The main contribution of this work was to identify and to emphasise the mechanisms leading to this anisotropic thermal expansion. In fact, and generally in aluminium silicates, whereas octahedra of aluminium present a significant expansion with temperature, tetrahedra of aluminium or silicon present a much lower expansion. In addition, in the case of andalusite, when aluminium is in coordinance five, the four shortest connections remain relatively unchanged, while the fifth longer one, significantly increases.

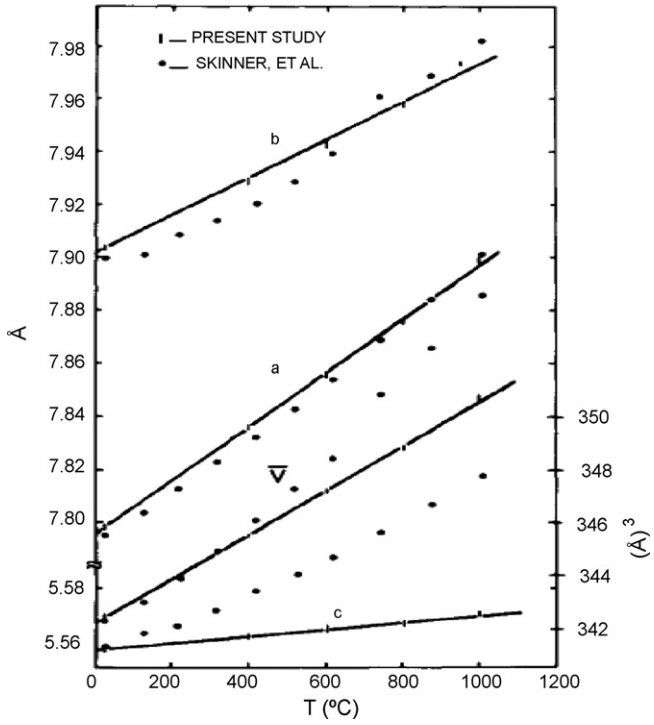


Fig. 4. Andalusite unit-cell dimensions and volumes as a function of temperature[14].

Globally, rigid tetrahedra of aluminium and silicon, and more flexible octahedra of aluminium, control the thermal expansion of the unit-cell of andalusite and lead to this strong anisotropy.

2.1.2. Studied material

The present study has been carried out on two kinds of andalusite particles. The first one is called Kerphalite (KB) from DAMREC Company, France. This is a classical raw material used to formulate andalusite-based refractories. The second one is call KI from ASACO Company, Iran. This is not a conventional raw material for refractory production but these andalusite single crystals offered much interest in the case of the present study. These two materials have quite similar compositions (Table 1), but, due to the small grain size available for KB (a few millimetres, Fig. 5a), the study on the anisotropy properties was carried out on KI crystals, which offer the advantage to be much larger (a few centimetres length, Fig. 5b).

2.2. Thermal expansion measurement

The dilatometric tests were carried out on a ADAMEL DI dilatometer. The samples usually used are of dimension

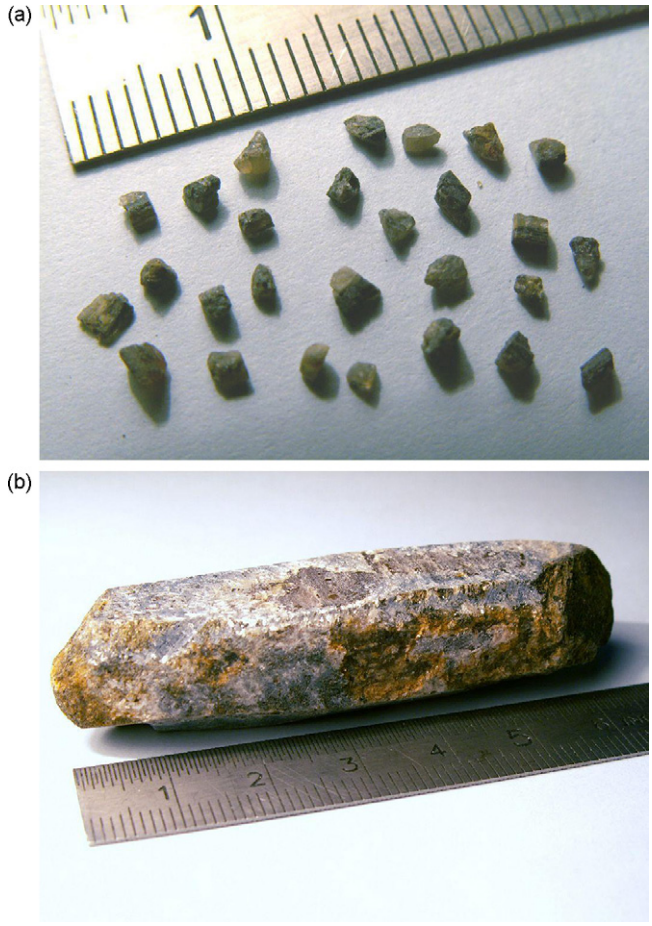


Fig. 5. Andalusite crystals: (a) KB and (b) KI.

10 mm × 5 mm × 5 mm. Thermal cycles are characterised by a 5 °C min^{-1} heating and cooling rates.

Two different types of sample were considered. To characterise the anisotropy of the thermal behaviour of a single crystal of andalusite, samples were directly cut in a KI single crystal according to the cutting scheme (Fig. 6). To characterise the dilatometric behaviour of andalusite polycrystals, samples issued from KB and KI powders (granulometry lower than 200 μm), were pressed (100 MPa) with a clay binder (bentonite 5%).

3. Results and discussion

Several additional phenomena can notably affect the intrinsic thermal expansion behaviour of andalusite particles. The first one is related to the presence of specific impurities within these crystals, in particular quartz inclusions which classically

Table 1
Chemical composition of the KB and KI andalusite crystals

	Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2	MgO	Na_2O	K_2O	Other
KB (wt%)	54.1	42.2	1.36	0.11	0.25	0.21	0.12	0.5	1.15
KI (wt%)	57–59	37–40	0.7	0.11	–	0.2	0.1	0.8	1.1–2.1

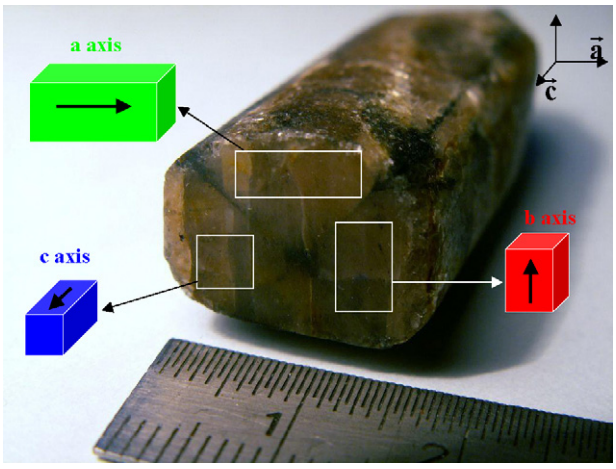


Fig. 6. Scheme of the dilatometric sample extraction procedure applied on an andalusite single crystal to investigate its thermal expansion anisotropy.

exhibit a large reversible thermal expansion in the 450–600 °C temperature range. The second one is an irreversible expansion associated to the mullitisation process above 1280 °C.

In the case of pressed powder samples, an additional shrinkage can also occur in the 1000–1500 °C temperature range, due to sintering.

Since the present work is focused on intrinsic thermal expansion behaviour of andalusite (mullitisation of andalusite grains is already well documented in literature Refs. [10,11]), we decided here to present and to comment results dealing specifically with expansion of these aggregates in their initial andalusite state and in their final mullitised state.

3.1. Dilatometric behaviour of aggregates in their "andalusite state"

The thermal expansion behaviour is presented here (up to 900 °C) on andalusite single crystal (Fig. 7a) and polycrystal (Fig. 7b). In order to avoid disturbances due to quartz dilatometric anomalies between 450 °C and 600 °C, which can occur beyond 500 °C, values of the coefficient of thermal expansion (CTE) were calculated in the 25–300 °C temperature range.

Table 2 summarises the different CTE values obtained in the considered temperature range for the aggregates.

Several observations, concerning this table, can be done. Firstly, one can easily note, on single crystal samples, the large difference of CTE values measured along the three crystallographic axis. These values are in good agreement with those previously reported in the literature[14]. A slight difference is

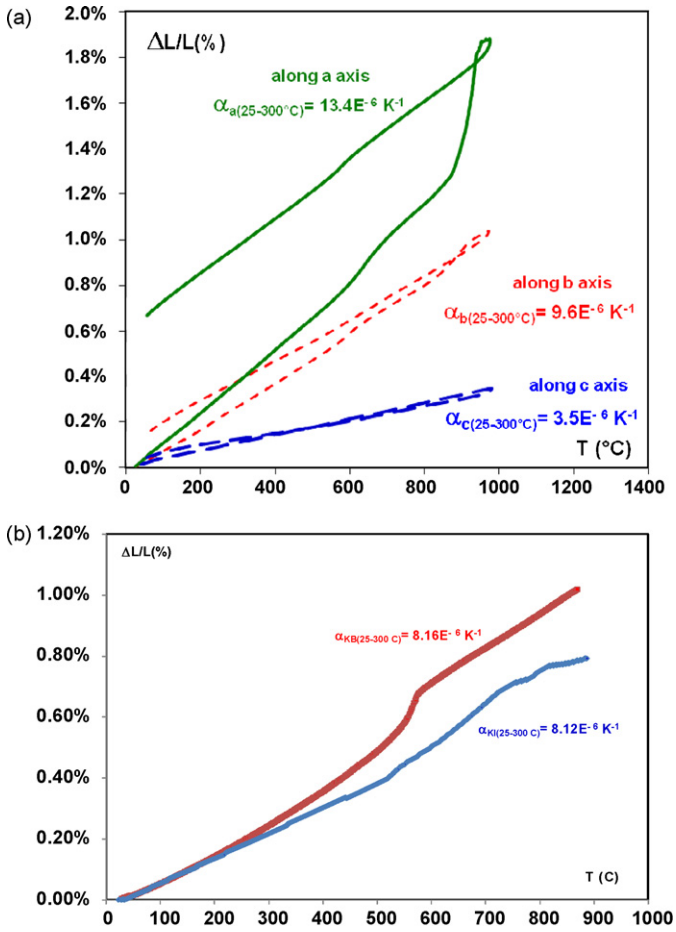


Fig. 7. Dilatometric behaviour of andalusite aggregates in their "andalusite state": (a) results obtained in the three directions for KI single crystal and (b) comparison of dilatometric behaviour between KB and KI polycristals.

however observed, but it is important to remember that the values reported by Winter and Ghose[14] have been obtained by XRD on powder of pure andalusite crystals. Anyway, these results highlight the marked anisotropy of the thermal expansion behaviour of andalusite aggregates. Secondly, concerning the polycrystal samples (KI and KB), one can observe the very close values obtained, which confirms their similar behaviour. One can also note that these values are quite close to the average value ($\bar{\alpha}_{KI} = 8.83 \times 10^{-6} K^{-1}$) calculated from the CTE values measured along the three axis and in addition, an "expansion effect" can be observed in Fig. 7a and b around 600 °C, both for polycrystals and single crystal samples. As previously mentioned, this effect can be attributed to the presence of quartz inclusions which exhibit a phase transformation from α (trigo-

Table 2
Coefficients of thermal expansion (α in 10^{-6} K^{-1}) of andalusite aggregates

Polycrystal		Single crystal (KI)			
KB	KI	Along *a* axis (Ref And. axis)	Along *b* axis (Ref And. axis)	(Ref And. axis)	$\bar{\alpha}_{KI}$
8.16	8.12	13.4	9.6	3.5	8.83
			Literature[14]		
	–	12.82	9.71	2.16	8.23

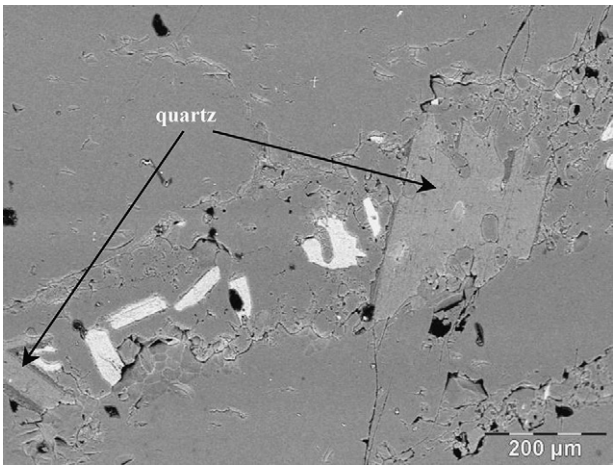


Fig. 8. Micrographies of quartz impurities located in the central cross of an andalusite aggregate.

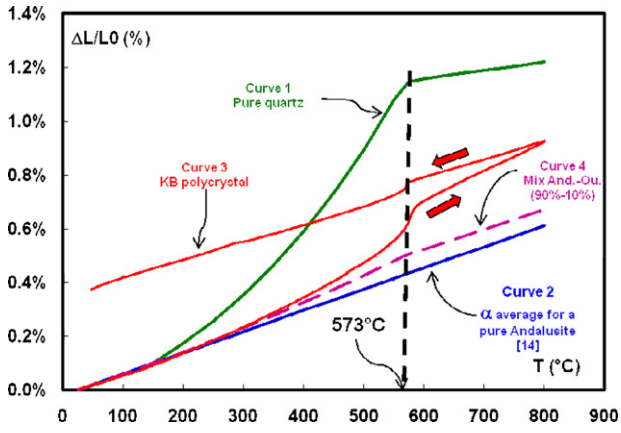


Fig. 9. Comparison of the thermal expansion evolution of materials containing more or less quartz.

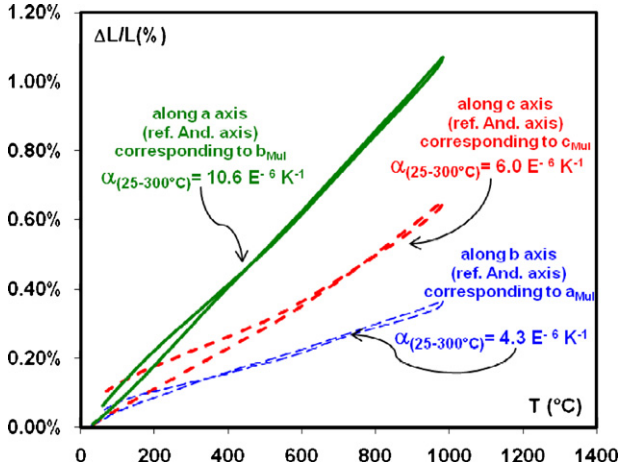


Fig. 10. Dilatometric behaviour along the three crystallographic axes for KI material obtained after mullitisation at 1500° C.

nal) to β (hexagonal) at 573 °C. Indeed, quartz inclusions are commonly observed as impurity in the characteristic central cross of andalusite crystals (Fig. 8).

In Fig. 7b, one can see that this "quartz effect" seems to be more significant for KB polycrystals than for KI ones. This matter of fact can be explained by the following. Considering the chemical composition of both materials indicated in Table 1, a simple calculation, based on an equimolar repartition of alumina (Al_2O_3) and silica (SiO_2) required for a pure andalusite, can easily show that a higher content of silica (up to 20 wt%) is available for quartz impurities formation in the case of KB andalusite crystals. Thanks to the supplier of this material (DAMREC Company), the announced amount of quartz as impurities seems to be about 5–10 wt%. At this stage, it is also important to note that a significant amount of silica might also be included in other impurities (biotite, ilmenite). In order to evaluate in "the most quantitative way possible" the effect of this relative amount of quartz in andalusite aggregates, Fig. 9 presents the thermal expansion evolution of different materials containing more or less quartz.

In this figure, four curves have been plotted. Curve 1 refers to the dilatometric behaviour of pure quartz polycrystals[15]. Curve 2 has been plotted on the basis of an average value of α (in order to be coherent with a polycrystal approach) extracted from the literature[14] for pure andalusite. The thermal expansion variation of KB has been re-plotted (curve 3). For comparison, the thermal expansion of a theoretical mixture of andalusite and quartz with the same composition as that of the KB polycrystal has been plotted (curve 4 in dash) by using a basic mixture law (Eq. (1)) with data for andalusite and quartz extracted from literature [14,15].

$$[(\Delta L/L)]_{mix}(T) = v_{Q}[(\Delta L/L)]_{Q}(T) + v_{And}[(\Delta L/L)]_{And}(T) \quad (1)$$

where $(\Delta L/L)(T)$ corresponds to the thermal expansion behaviours, v to the volume fraction and Q, 'And' and 'mix' indices referred to quartz, andalusite and mixture, respectively. The analyse of curve 4 compared to the one which refers to the KB material (curve 3) shows an exaggerated expansion compared to the real content of quartz given by DAMREC. Even if the basic mixture law which has been applied here does not take into account the stiffness evolution of the constituents[16,17], the observed difference seems to be significant. An attempt to explain this could deal with the localisation and the relative orientation of quartz in andalusite aggregates. Indeed, the thermal expansion mismatch which exist between these two phases can induce strong internal stresses leading to an additional damage. One clue which can be given to support this hypothesis is that an irreversible evolution of the thermal expansion along each axis of the single crystal (more marked for and axis) is observed (Fig. 7a). This non-reversible behaviour according to the thermal cycle indicates the possible occurrence of a damage due to a specific state of stress within the particle leading to the non return to zero of the curve at the end of the thermal cycle.

3.2. Dilatometric behaviour of aggregates in their "mullitised state"

Since refractory materials are regularly subjected to temperature above 1500 °C, andalusite aggregates are finally very often

Table 3
Coefficients of thermal expansion (α in $10^{-6}\,K^{-1}$) of andalusite aggregates in their initial and mullitised forms

	Along *a* axis (Ref And. axis)	Along *b* axis (Ref And. axis)	Along *c* axis (Ref And. axis)
Andalusite state	13.4	9.6	3.5
Mullitised state	10.6 (*b* axis in Ref. Mull)	4.3 (*a* axis in Ref. Mull)	6.0 (*c* axis in Ref. Mull)

in their mullitised state. In order to characterise the dilatometric behaviour in this final state, measurements have been carried out on samples previously treated during 30 min at 1500 °C to achieve a complete mullitisation. Fig. 10 shows the thermal expansion behaviour of a mullitised KI single crystal, along each crystallographic axis and Table 3 compares the calculated values of the CTE obtained in the 25–300 °C temperature range before and after mullitisation.

The first observation which can be made is that the anisotropic character of the thermal expansion behaviour is preserved. In comparison with previous results obtained in "andalusite state", a significant variation of the CTE values is however noted (decrease of α along *a* and *b* axis, increase of α along *c* axis). In the same time, Fig. 10 shows a quasi-reversible evolution of the thermal expansion for the three axes (at least more reversible than the one observed for non-mullitised andalusite; Fig. 7a).

In fact, during mullitisation treatment, the grain shape and the bulk chemistry are retained; a single crystal grain is converted into a composite made of a mullite crystals with a capillary network filled with silica rich glass[18–21]. The transformation is a complex mechanism with the preservation of octahedra, decomposition and rearrangement of the other structural entities. According to single crystal X-ray diffraction studies[12,13], the transformation from andalusite to mullite proceeds in a topotactical reaction leading to the followed orientation relationship: a_{Mul} axis parallel to b_{And} axis, b_{Mul} axis parallel to a_{And} axis, and c_{Mul} axis parallel to c_{And} axis. An SEM observation of a mullitised grain after a surface attack with hydrofluoric acid (Fig. 11a) reveals the network of mullite crystals with their *c* elongated axis parallel to the initial *c* andalusite one.

In the same time, the silica glass induced by the mullitisation fills the interstices of the mullite network but also exudes at the surface of the aggregates due to the expansion associated to the reaction (Fig. 11b). At the end, the mullitisation of pure andalusite aggregate leads to a two phases composite constituted of about 83 vol.% of mullite and 17 vol.% of silica glass. In our case, quartz impurities as inclusions in the native andalusite aggregate, which are probably transformed to a glassy phase during the 1500 °C treatment, might increase the final silica glass ratio. The absence of any quartz effect on dilatometric curve of mullitised samples (Fig. 10) confirms that hypothesis.

Considering the relation which should exist between the initial crystallographic axis of the andalusite aggregate and the final crystallographic axis of the mullite network, the CTE values reported in Table 3, for the mullitised state, should be related to the average CTE value calculated from literature [22–24] for a mullite single crystal: $4.15 \times 10^{-6}\,K^{-1}$, $6.17 \times 10^{-6}\,K^{-1}$ and $6.15 \times 10^{-6}\,K^{-1}$ along the *a*, *b* and *c* crystallographic axis, respectively.

Even if the measurement in the *a* direction (referred in the initial andalusite axis) is very high compared with the value obtained in the corresponding *b* direction for mullite single crystal, it appears that the measurements in the others directions are in very good agreement with values in the corresponding directions for mullite single crystal.

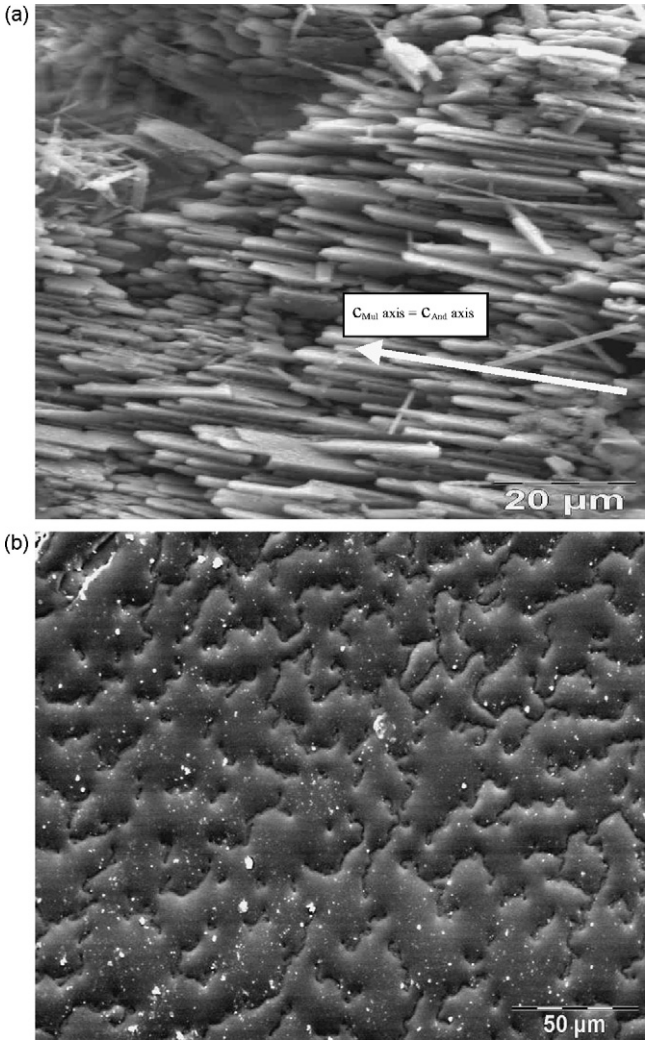


Fig. 11. Micrographies of a mullitised andalusite grain, 30 min at 1500° C: (a) mullite network formed within the grain revealed by hydrofluoric acid (HF) surface attack and (b) exudation of silica on the surface of the grain.

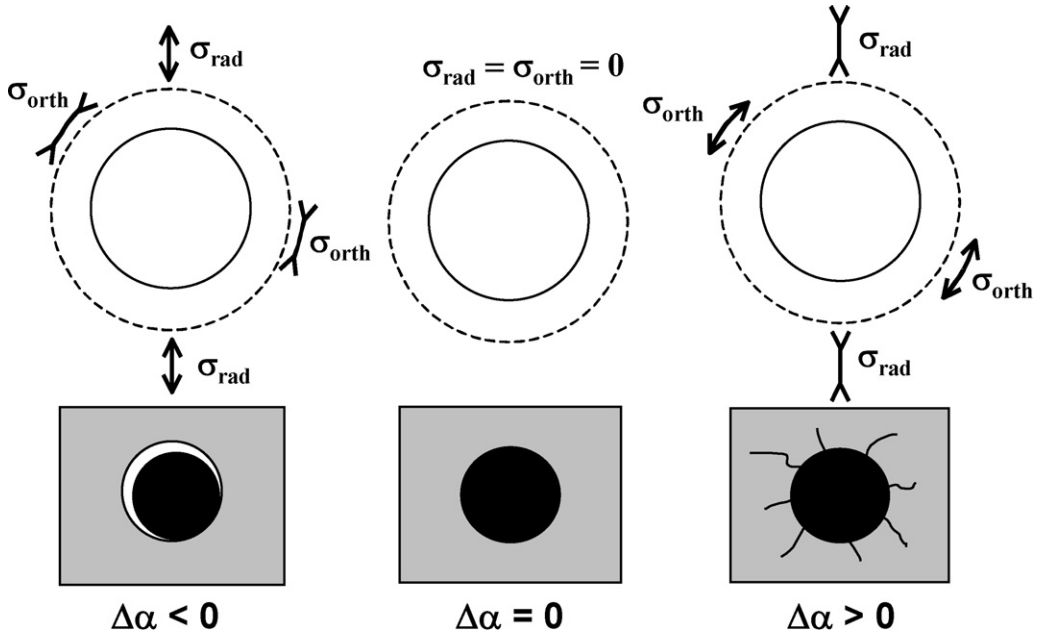


Fig. 12. Internal stresses and associated damage mechanisms involved during cooling by thermal expansion mismatch between phases within a model material containing spherical inclusions embedded in an infinite isotropic matrix.

3.3. Contribution of the anisotropic thermal expansion behaviour of andalusite aggregates to induce diffuse damage in refractory castables

As mentioned in the introduction of this paper, the ability of refractory materials to develop a tailored network of microcracks within the microstructure constitutes a key point to promote thermal shock resistance. Assuming a refractory as a two phase model material[1] constituted by a matrix (CTE = α_m) and aggregates (CTE = α_a) both supposed, in a first step, to be isotropic constituents, three different configurations concerning microstructural damage can be obtained, according to the CTE mismatch existing between the matrix and aggregates ($\Delta\alpha = \alpha_m - \alpha_a$), as presented in Fig. 12:

- when $\Delta\alpha < 0$, the contraction of the matrix (during cooling after sintering) is lower than that of aggregates. The interfaces between matrix and aggregates is thus stressed in radial tension and in tangential compression. The intensity of the tensile stress can lead to partial or total interfacial debonding.
- when $\Delta\alpha = 0$, no stress appears at the interface since matrix and aggregates contract in same way.
- when $\Delta\alpha > 0$, the contraction of the matrix is higher than that of aggregates. The interfaces between matrix and aggregates is thus stressed in radial compression and in tangential tension. In this case, the intensity of the tangential tensile stresses can lead to radial microcracks of the matrix around the aggregates.

Considering this simple classical approach based on isotropic constituents, the case of refractory castables with andalusite aggregates should be analysed by taking into account the CTE

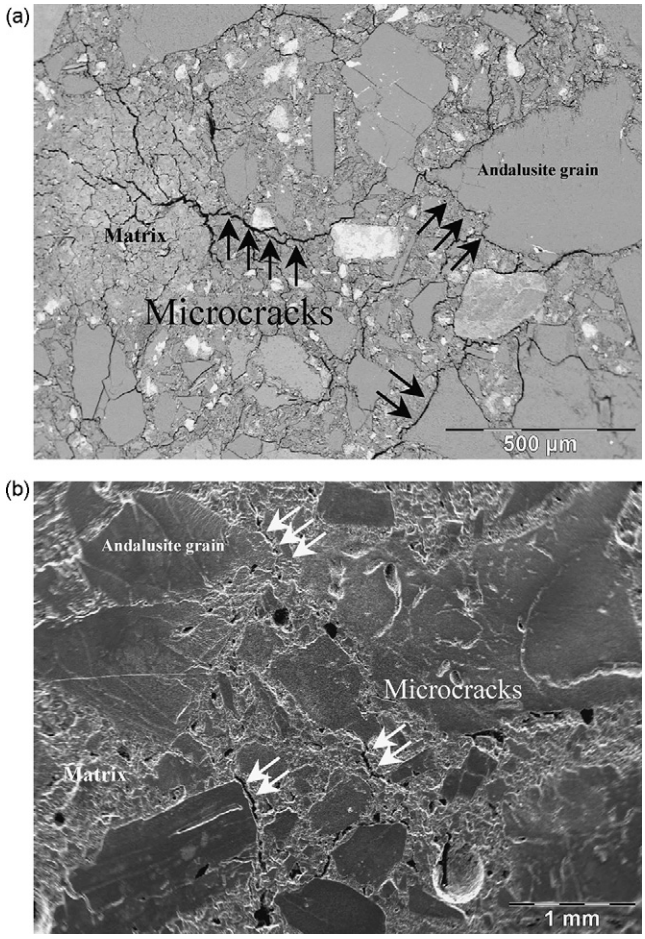


Fig. 13. SEM image of a polished section of andalusite castable: numerous microcracks observed in the material after firing at different temperatures: (a) 900° C and (b) 1500° C.

value for the fine part of the castable containing cement, silica fume and alumina (typically $7.6 \times 10^{-6}\,K^{-1}$ for particle size lower than 200 μm[25]), and the CTE of andalusite aggregates taken in their polycrystal form (typically $8.16 \times 10^{-6}\,K^{-1}$ in the case of KB)

Since these values are relatively close, $\Delta\alpha$ is, in this case, nearly equal to zero ($\Delta\alpha = -0.56 \times 10^{-6}\,K^{-1}$). This means that very limited stress should appear at the interface since matrix and aggregates contract nearly in the same way.

On the other hand, numerous microcracks located both at the aggregates/matrix interfaces and within the matrix have been observed (Fig. 13a) in the castable after intermediate temperature thermal cycle (typically 900 °C).

If we consider now the level of real damage induced in the microstructure, we must in fact take into account the three distinct values of the CTE along each crystallographic axis. Considering this anisotropy of thermal expansion, and the different values of CTE (Table 2), one can easily see that $\Delta\alpha$ is sometimes strongly negative ($\Delta\alpha$ with α_a along a-axis $= -5.8 \times 10^{-6}\,K^{-1}$), leading to partial or total interfacial debonding, and sometimes strongly positive ($\Delta\alpha$ with α_a along c axis $= +4.1 \times 10^{-6}\,K^{-1}$) leading to radial microcracks of the matrix around the particles.

After mullitisation, the CTE mismatches between matrix and aggregates become a little bit lower ($\Delta\alpha$ with α_a along b_{Mul} axis $= -3.0 \times 10^{-6}\,K^{-1}$ and $\Delta\alpha$ with α_a along a_{Mul} axis $= +3.3 \times 10^{-6}\,K^{-1}$). Then, the microcracks density observed after a thermal cycle up to 1500 °C (Fig. 13b) is logically lower than the one induced by a thermal cycle at an intermediate temperature (Fig. 13a). This is also confirmed by the decrease of elastic property values during the cooling stage, well known as a good marker of the level of damage, which was found to be more important in the case of thermal treatment carried out at intermediate temperatures[4].

4. Conclusion

Difference of thermal expansion between the constituents of refractory materials can lead, during heating and cooling stages, to the development of a large microcracks network within the microstructure, which strongly affects the thermo-mechanical properties: thermal expansion coefficient, Young's modulus and stress–strain law.

The availability of andalusite single crystals of important size allowed us here to characterise the dilatometric behaviour, before and after mullitisation, according to various crystallographic axes of the andalusite aggregates. A strong differential of dilation thus could be identified in these aggregates in their initial form but also in their mullitised form, taking into account the topotactic character of this transformation. Consequently, this strong anisotropy of dilation is probably at the origin of the marked damage induced by thermal cycles corresponding to application conditions. The single crystal character of andalusite aggregates involves a very strong anisotropy of thermal expansion, which leads to a large CTE mismatch with the cementitious matrix. Through a good knowledge and an accurate control of such microstructural mechanisms, one can take advantage of the resulting enhancement of compliance and strain to rupture for applications with thermal shock conditions. These results constitute, indeed, a significant base which confirms previous proposed interpretation concerning the mechanical behaviour in tension of andalusite-based castables[4–6].

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