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Mullite grown from fired andalusite grains: the role of impurities and of the high temperature liquid phase on the kinetics of mullitization and consequences on thermal shocks resistance

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Abstract

Mullitization and microstructure of mullite grown from fired andalusite grains has been studied in the literature. Mechanisms of mullite formation are well known: during heating, andalusite single crystal grains are transformed into a composite made of a 3:2 mullite single crystal with a capillary network filled with silica rich liquid. But very few works studied the influence of the impurities on the kinetics of mullitization. This paper shows that the presence of impurities (mainly iron and alkalis) in the andalusite increases the amount of the liquid phase and decreases the liquid viscosity. The mullitization kinetics depends on the andalusite grain size, the chemical composition, the origin of the andalusite deposit and the amount and the properties of the liquid phase. Because of the specific microstructure and the presence of the liquid phase, during thermal shocks in air, the mullitized andalusite crystals exhibit a behaviour typical of composite materials: microcracks are deflected by mullite/glass interfaces and stopped in glass zones. During a further heating, cracks generated by a thermal shock are healed.

Keywords: B. Microstructure; Kinetics of mullitization; Thermal shocks; D. Mullite; Andalusite

1. Introduction

Mullite exhibits attractive properties for refractory ceramics: high refractoriness, low thermal conductivity, low thermal expansion, good chemical stability and interesting mechanical properties at high temperatures. Refractories with high mullite content may be achieved by firing natural andalusite as raw material.

Andalusite ($Al_2O_3SiO_2$) is a natural mineral found in low-grade metamorphic rocks.

Andalusite concentrates are available as granular particles ranging in size up to 8 mm. Each grain is made of a single crystal or fragment of single crystal. Andalusite content of concentrates range usually around 90–95% and their main mineral impurities are quartz, biotite, sericite, ilmenite, pyrite, etc.

During heating, andalusite is converted into 3:2 mullite ($3Al_2O_3$–$2SiO_2$) and silica rich glass. Complete transformation leads to about 80% mullite and 20% glass.

Mullitized andalusite grains exhibit specific microstructure characteristics. During heating, the grain shape and the bulk chemistry are retained; a single crystal grain is converted into a composite made of a 3:2 mullite single crystal with a capillary network filled with glass [1] (cf. Fig. 1). Mullite is topotactically oriented in relation with the host crystal with its *c* axis parallel to the *c* axis of the initial andalusite [2–4].

The glass filled capillaries form highly interconnected tubes with diameter in the micrometer range and are elongated along the *c* axis common to the neoformed mullite and the parent andalusite crystal.

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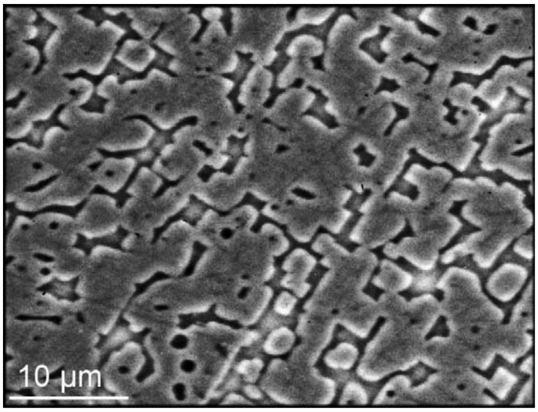


Fig. 1. Mullite-glass composite formed by heating an andalusite crystal at 1600 °C. Backscattered electrons SEM micrograph on polished section approximately parallel to the (0 0 1) plane of the initial andalusite crystal.

The glass is silica rich and its composition differs only slightly from that of the eutectic liquid in the pure Al_2O_3–SiO_2 system: SiO_2 ≈91% and Al_2O_3 ≈9% [5]. This glass contains iron (Fe_2O_3 ≈1–3%), potassium (K_2O ≈1–3%) and other elements with amounts below 1% initially inside the minor impurity phases included in andalusite.

As in the binary Al_2O_3–SiO_2 system, the lowest eutectic occurs at 1587 °C, mullitization of andalusite below that temperature was classically considered to be a solid state reaction leading to a great number of mullite needles oriented in relation with the host crystal [3,6].

Owing to impurities in the concentrates, mainly alkalis and iron, local melting may occur at low temperature. The presence of a liquid generated by low-temperature melting of impurities (quartz, various sheet silicates, ilmenite, iron oxide generated by the oxidation of pyrite) contained in the andalusite grains plays an important role. Impurities are mainly located on the surface of grains, in altered stripes following primary cracks or opened cleavages, and in the chiastolitic cruciform patterns. Formation of a liquid phase promotes atomic diffusion and allows mullitization to occur through a dissolution–precipitation mechanism [1,4].

Mullitization starts in inclusion rich zones and reaction rims grow from the surface of the grain as well as from cracks or perturbed zones. Because of the topotactic relations between mullite and andalusite, all nuclei have the same orientation and coalesce as they grow, entrapping part of the surrounding liquid. The mullite single crystal grows at the expense of the low-temperature phase and invades progressively the whole grain.

The transformation of andalusite in a composite made of mullite single crystal with a capillary network filled with silica rich glass at high temperature was studied and the dissolution–precipitation mechanism involving silica rich liquid was established [1,4]. But the influence of the impurities in the initial andalusite on the properties of the liquid phase and on the kinetics of mullitization is not well known.

The purpose of this paper is to investigate the role of the impurities and the high temperature liquid associated with the mullite formation on the kinetics of mullitization of andalusite grains and the behaviour of fired andalusite grains submitted to thermal shock.

2. Experiments

Mullitization kinetics were studied for temperatures ranging from 1200 to 1600 °C and for several calibrated andalusite sands, with mean dimensions of 5, 55, 200 and 1500 μm, supplied by DAMREC. The quantitative mineral composition of the concentrates may be evaluated from their chemical composition by a calculation similar to that for the petrological norm of a rock. This calculation takes into account theoretical andalusite, quartz, ilmenite, anorthite and a typical mica with the following structural formula: $(K,Na)(Fe_xMg_yAl_{2-3(x+y)/2})(AlSi_3O_{10})(OH)_2$. Chemical compositions of the used andalusite concentrates are given in Table 1.

Thirty grams of grains were placed in alumina crucibles and were heated for the required time using a temperature and time controlled electrical furnace. Heating rates were close to 900 °C/h. For each sample, the amount of mullite was determined by X-ray quantitative analysis, using eskolaïte (Cr_2O_3) as internal standard and reference mullite samples with known 3/2 mullite amounts. The relative error of the measurements is estimated to be maximally ±5%.

Table 1
Chemical composition and computed theoretical andalusite content of the used andalusite concentrates (mass%)

	5 μm	55 μm	200 μm	1500 μm, D1	1500 μm, D2	1500 μm, D3	1500 μm, D4
Al_2O_3	62.70	60.25	61.90	61.14	60.41	60.38	60.56
SiO_2	36.36	38.76	37.50	37.89	38.12	38.48	38.33
Fe_2O_3	0.50	0.54	0.40	0.57	0.79	0.59	0.59
TiO_2	0.11	0.13	0.10	0.15	0.21	0.17	0.21
CaO	0.06	0.06	0.04	0.04	0.10	0.09	0.08
MgO	0.15	0.06	0.01	0.07	0.08	0.07	0.06
Na_2O	0.01	0.02	0.03	0.01	0.05	0.01	0.01
K_2O	0.11	0.18	0.01	0.13	0.24	0.20	0.16
Computed andalusite content	96.43	95.40	98.18	96.68	95.46	94.97	95.44

Table 2
Maximum mullite amount for complete mullitization of the andalusite concentrates

	5 μm	55 μm	200 μm	1500 μm, D1	1500 μm, D2	1500 μm, D3	1500 μm, D4
Mullite amount for complete mullitization (%)	80.2	79.4	81.7	80.4	79.4	79.0	79.4

3. Results

The rate of mullitization for each fired andalusite concentrate is computed from the mullite content determined by X-ray quantitative analysis: it corresponds to the amount of mullite determined by X-ray quantitative analysis divided by the maximum mullite amount for complete mullitization (cf. Table 2).

Despite the fact that X-ray data only reveal diffraction of 3/2 mullite for whole fired samples, the presence of a glass involves that complete reaction leads to a mullite content significantly less than 100%. Mullite amounts for complete mullitization depend on the initial andalusite content. They are given in Table 2; they were calculated from chemical compositions and range from 79.0% (1500 μm, D3) to 81.7% (200 μm).

The present results are in accordance with those obtained by Schneider and Majdic [6]. They found that mullitization of andalusite powders becomes effective at 1280 °C, but with a slow reaction rate, and that the reaction rate increases significantly above 1380 °C. Our study reveals that mullitization can occur at lower temperatures: with 5 μm grains, mullite was detected after 48 h heating at 1100 °C. At 1100 °C, the transformation is very slow, and we were not able to quantify the amount of mullite (lower than 1% after 80 h).

Fig. 2 summarizes the results for the 200 μm andalusite grains. It shows the evolution of the amount of mullitization versus the soaking time. At 1600 °C, mullitization is very fast and complete mullitization is achieved during the first hour soaking. At 1500 °C complete mullitization is reached only after 48-h soaking. Below 1500 °C, complete mullitization is not achieved during the 100-h soaking. For the lower temperatures, for example 1200 °C, the transformation of andalusite just begins; after a 100-h soaking, the amount of mullitization is about 2–3%.

4. Discussion

4.1. *Influence of the grain size and the origin of the andalusite on the kinetic of mullitization*

At temperature below 1500 °C, as mullitization is not too fast, the kinetics of mullitization depend on the grain size and on the origin of the andalusite. Fig. 3 shows the evolution of mullitization during the 1350 °C isothermal treatment for four andalusite grain sizes issued from the same deposit. Kinetics are faster for 5 μm grains than for the 55 μm ones and are slower for the 200 and 1500 μm andalusite grains which exhibit near the same mullitization rate. Kinetics of mullitization are always faster for the smallest andalusite grains.

As mullitization starts at inclusion rich zones and at the grain borders and invades the core of the grains, complete mullitization of a fine grain would be more rapidly achieved than complete mullitization of a large one. Because of defects and impurities distribution in andalusite, only grains smaller than ≈100 μm seem to be affected by a size effect.

Fig. 4 summarizes the results at 1350 °C for four 1500 μm andalusite grain sizes issued from different deposits. Complete mullitization is not achieved during the 100-h soaking.

As origin or grain sizes of andalusite are different, the amounts of impurities in the mineral concentrates are different. Impurities contained in andalusite grains, mainly iron and alkalis, generate local low-temperature local melting. The early-formed liquid phase promotes diffusion

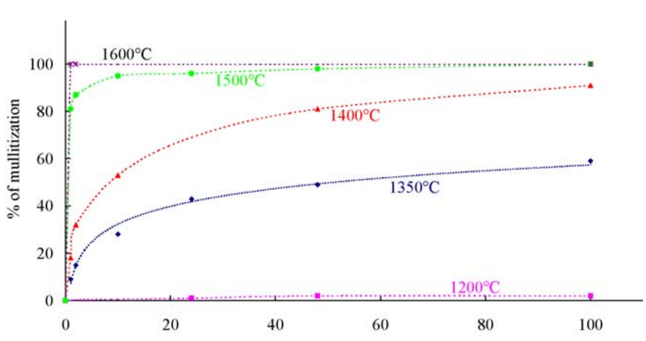


Fig. 2. Kinetics of mullitization of 200 μm andalusite grains for temperatures ranging from 1200 to 1600 °C.

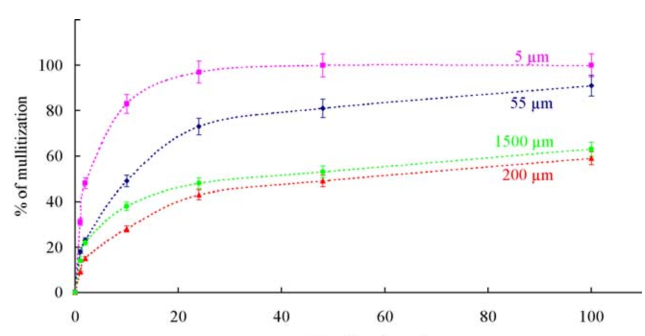


Fig. 3. Kinetics of mullitization at 1350 °C for four andalusite grain sizes issued from the same deposit.

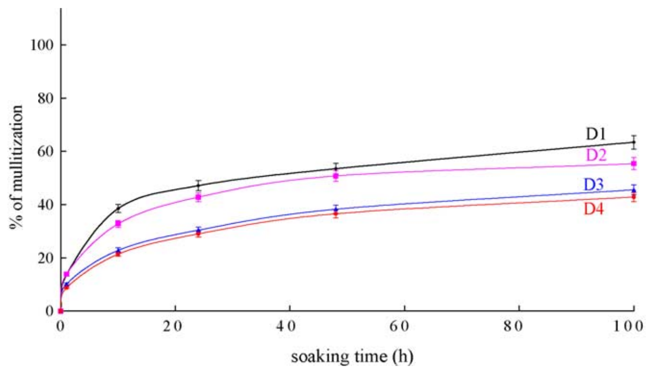


Fig. 4. Kinetics of mullitization at 1350 °C for 1500 μm andalusite grains issued from different deposits.

and dissolution–precipitation mechanisms. Two parameters related to the liquid phase may affect the kinetics of mullitization: the amount of liquid and its viscosity, which both depend on the amount of impurities of the initial andalusite. Fig. 5 shows that the amount of glass in the mullite-glass composite increases with the amount of impurities contained in the andalusite concentrates.

4.2. The role of the impurities on the viscosity of the liquid phase

E.D.S. chemical microanalysis of some large glass areas of different mullitized andalusite grains indicate that impurities are concentrated in the silica rich glass (cf. Table 3) and that the glass composition show local variations that may be attributed to the initial distribution of mineral impurities. Quite pure Al_2O_3–SiO_2 compositions, without detectable iron or alkalis, were found on mullitized grains of high purity andalusite without observable foreign inclusions (cf. Table 3, column 3); these glasses show the highest observed silica contents and are near the eutectic composition of the pure Al_2O_3–SiO_2 system.

The viscosity of the liquid phase at high temperature is related to the kind and the amount of impurities. The viscosity of glasses at given temperatures can be calculated

Table 3
Chemical composition glasses in mullitized andalusite grains (EDS analysis on polished section)

	Glass 1 (%)	Glass 2 (%)	Glass 3 (%)
SiO_2	76.7	77.4	86.0
Al_2O_3	19.3	18.6	14.0
Na_2O	0.6	0.5	<0.2
K_2O	1.4	1.3	<0.2
MgO	0.6	0.5	<0.2
Fe_2O_3	0.8	0.6	<0.2
CaO	0.6	1.1	<0.2

from their chemical compositions by the use of the model of Urbain et al. [7]. Fig. 6 shows the evolution of computed viscosities of liquid for a pure silica–alumina glass (yield by the mullitization of pure andalusite grains) and for a glass with impurities (issued by the mullitization of andalusite grains with some foreign inclusions).

Results show that the viscosities of both liquids decrease as the temperature increases and are very similar at temperatures above 1450 °C. Below 1450 °C, the influence of impurities increases and at 1200 °C, the viscosity of the liquid containing impurities becomes nearby half that of the pure silica–alumina glass.

One may conclude that the presence of impurities in the andalusite concentrates has three main effects:

- They lower the temperature of early formation of a liquid phase.
- They increase the amount of the liquid phase.
- They lower the viscosity of the liquid phase.

The three effects act together on the promotion of chemical transport and play an important role on kinetics of mullitization.

4.3. The role of the liquid phase on the thermal shock resistance

Mullitized single crystals of andalusite were submitted to thermal shock in air. Large well-formed crystals were

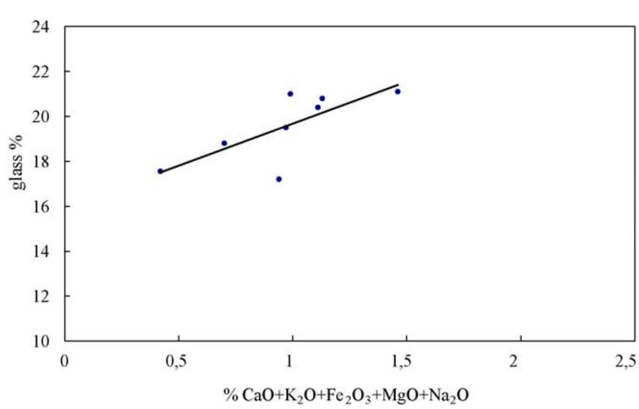


Fig. 5. Correlation of the glass content in the mullite-glass composite and the amount of impurities in the initial andalusite.

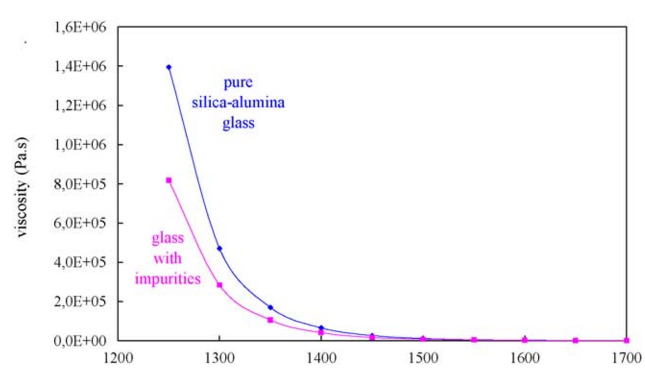


Fig. 6. Influence of the glass composition on the evolution of the liquid viscosity with the temperature.

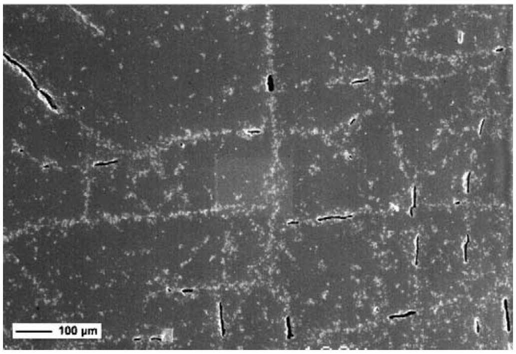


Fig. 7. SEM secondary electrons micrograph of a mullitized andalusite single crystal. Polished section cut parallel to the (0 0 1) plane of andalusite.

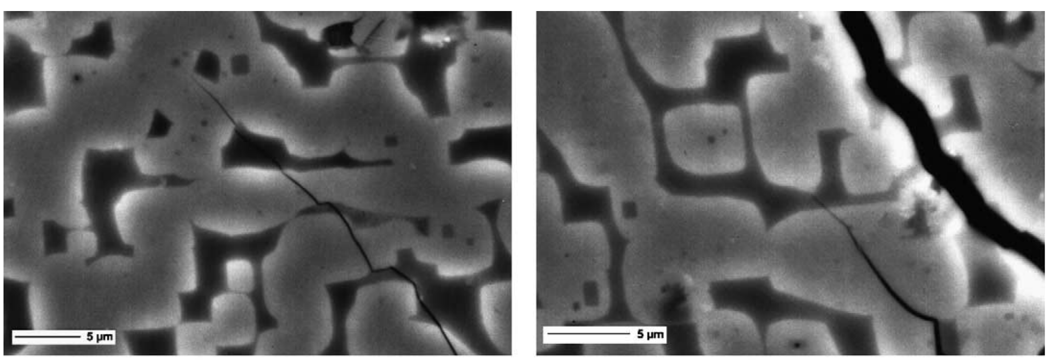
selected, carefully cleaned and heated for 2 h at 1600 °C for a complete mullitization. Crystals were cut perpendicularly to their c axis in order to obtain square slabs (about 6 mm × 6 mm × 3 mm) and one (0 0 1) face was polished.

Mullitized slabs were introduced in an electric furnace at 1200 °C. After temperature stabilization (about 10 min), pieces were submitted to a thermal shock. In order to increase quenching intensity, each sample was rapidly extracted from the furnace and its polished face placed on a cooled polished copper piece. Quenching duration from 1200 to 20 °C was less than 5 s (a quenching rate of about 236 °C/s).

Because of the direction of the main generated temperature gradient, cracking occurred perpendicular to the polished face.

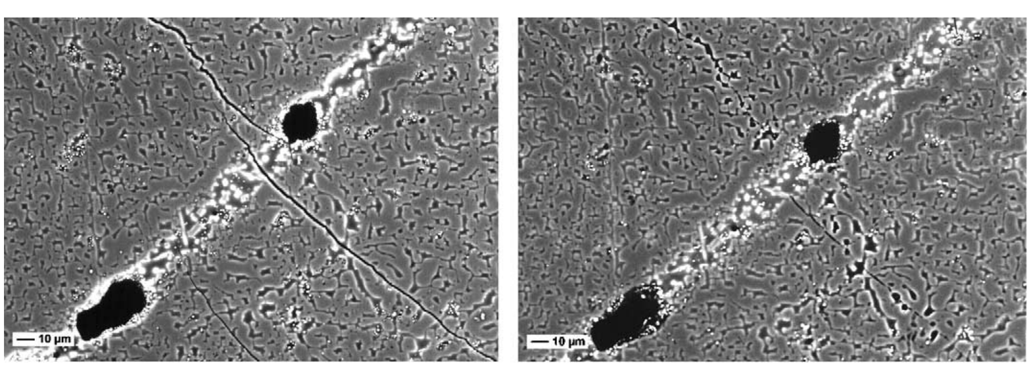
The polished faces were examined by SEM using secondary and backscattered electron imaging. Backscattering electron imaging with a high contrast proved to be much more effective for the observation of the thin tips of microcracks.

As andalusite is a natural mineral issued from a metamorphic stressed context, crystals exhibit an initial crack network with many cracks resulting from opening of the (1 1 0) cleavage planes. During mullitization, initial cracks of the andalusite crystals are healed by glass or/and by glass and mullite needles, and the mullite-glass composite appears uncracked. Healed initial cracks are marked by lines of glass-filled small pores and some of them are underlined by larger empty flattened vesicles (cf. Fig. 7).



(A) (B)

Fig. 8. Tips of a single crack (A) and of an echelon crack (B) in the mullite-glass composite after a thermal shock (backscattered electrons SEM micrographs on polished sections cut parallel to the (0 0 1) plane of initial andalusite).



(A) (B)

Fig. 9. (A) Echelon cracks generated by a first thermal shock in the mullite-glass composite. They cross a large fracture of the initial andalusite crystal that was healed during the mullitization of the grain. (B) Same zone but after a second heating at 1200 °C and a second thermal shock. The existing cracks are healed by the heating (backscattered electrons SEM micrographs).

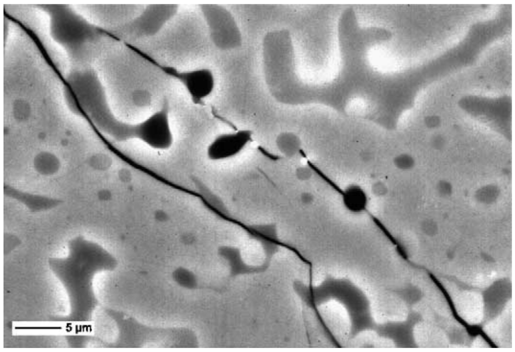


Fig. 10. Cracks generated by a second thermal shock (at the bottom) near the crack generated by the first thermal shock (at the top). The first generation crack is partially healed, and the new crack develops at the vicinity, with the same orientation, but with a more deviated path (back-scattered electrons SEM micrographs).

Small slabs never split during quenching and only a few cracks (1–3) were observed in each shocked sample. As expected, they are perpendicular to the polished face, and their length is about 3–4 mm. The maximum opening of the microcracks is about one micrometer. No relation was found between cracks produced in the composite by thermal shocks and the healed cracks of the initial andalusite crystal.

Mullitized andalusite single crystals exhibit a behaviour typical of composite materials concerning the propagation of microcracks: microcracks are deflected by glass-mullite interfaces and stopped in glass zones (cf. Fig. 8).

Some slabs were submitted to a second thermal shock by repeating the same procedure as for the first one (1200 °C, 10 min annealing, quenching rate about 365 °C/s). SEM examination revealed that during the 10 min heating at 1200 °C, the existing cracks were almost cured (cf. Fig. 9). In the largest opened zones, the walls of cracks are filled with glass, and in the thin parts, the mullite crystal continuity seems to be restored.

After a second thermal shock, new cracks are generated with the same characteristics as the first ones. Second generation cracks may be new fractures without any relation to the former or they may follow the trace of the first generation cracks. In the last case, the first generation crack is not reactivated and the new crack develops separately (cf. Fig. 10). So, the second generation cracks show a less linear path than the first generation ones.

5. Conclusion

By firing natural andalusite grains as starting material, a $3Al_2O_3$–$3SiO_2$ mullite is formed by a dissolution–precipitation mechanism involving silica rich liquids issued by low-temperature melting of impurities. Andalusite single crystal grains are transformed into a composite made of mullite single crystal with a capillary network filled with silica rich glass.

In spite of a high glass content, and as a result of trapping of the main part of the glass in the capillary network of the mullite composite crystals, andalusite based refractories exhibit outstanding physical and chemical properties [8]. When faced with aluminium killed steel, andalusite made ceramics have shown very slow silicon uptake by the steel, and behave like refractories much richer in alumina [9].

This paper shows the significant role of the impurities (mainly iron and alkalis). The presence of impurities in the andalusite concentrates increases the amount of the liquid phase, decreases the liquid viscosity, and therefore promotes atomic mobility. Because of the initial distribution of impurities in the andalusite grains, combined with the enhancing effect of the liquid phase on chemical exchanges, kinetics of mullitization depend on the andalusite grain size, on the chemical composition and on the origin of the andalusite deposit. These effects have to be taken into account during the industrial firing of the andalusite made bricks or castables in order to obtain a complete mullitization.

The presence of a liquid phase plays an important role on the behaviour of fired andalusite grains submitted to thermal shocks.

During the mullitization, the liquid phase heals initial cracks of the andalusite grains, then the mullite-glass composite appears uncracked.

The mullitized andalusite crystals exhibit a typical behaviour of composite materials: microcracks are deflected and stopped in glass zones.

Each further heating treatment leads to some healing of the existing cracks.

The specific microstructure of mullitized andalusite leads to excellent thermal shock resistance in comparison with monocrystalline mullite [8]. It shows a good creep behaviour in thermal cycling between 1000 and 1500 °C, compared with bauxite bricks [10]. Therefore, andalusite made refractories are well suited for a thermal cycling use. These results offer new possibilities for the development of refractories using andalusite raw materials with optimized microstructure.

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