



Effects of Alumina Powder Characteristics on the Reactive Sintering of CaO-Al₂O₃

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Abstract

The microstructure of fired materials resulting from the reactive sintering of mixtures in the system alumina–lime depends on the characteristics of the starting components. This work aims to better understand the effect of some characteristics of the starting component of alumina (specific surface area, particle size distribution, morphology, impurities) on the microstructure evolution during thermal treatments of materials in the system Al₂O₃-CaO.

Keywords: Alumina, Calcium aluminate, Reactivity, Microstructure, Impurities, Specific surface area

WPŁYW CHARAKTERYSTYKI PROSZKU KORUNDOWEGO NA SPIEKANIE REAKCYJNE CaO-Al₂O₃

Mikrostruktura materiałów wypalonych wynikająca z reakcyjnego spiekania mieszanin w układzie tlenek glinu – tlenek wapnia zależy od charakterystyki składników wyjściowych. Celem tej pracy jest lepsze zrozumienie wpływu niektórych charakterystyk tlenku glinu, jako składnika wyjściowego, (powierzchnia właściwa, rozkład wielkości cząstek, morfologia i zanieczyszczenia) na ewolucję mikrostruktury podczas obróbki cieplnej materiałów w układzie Al₂O₃-CaO.

Słowa kluczowe: Al₂O₃, glinian wapnia, reaktywność, mikrostruktura, zanieczyszczenia, powierzchnia właściwa

1. Introduction

To study the effect of alumina characteristics on the physic-chemical properties of the system CaO-Al₂O₃, some bimodal mixtures were realised by mixing an alumina powder and a calcic phase (CA = CaAl₂O₄, CA₂ = CaAl₄O₇, or C₁₂A₇ = Ca₁₂Al₁₄O₃₃) and finally formed by pressing. The microstructural characteristics of these model materials resulting from reactive sintering between these two components were studied. The temperature range of heat treatments is between 900 and 1260°C. There is in the literature some information about the influence of specific surface area and impurities of alumina on the sintering behaviour of an alumina material. But in this study, the objective is to determine if the characteristics of alumina have an influence on the reactivity and microstructure evolution of materials made from alumina and those of calcium aluminates. We have shown in this study that the specific surface area, the morphology and the impurities of the alumina particles can affect these properties, specially the reactivity of the system.

2. Experimental

Different alumina powders were used in order to study the influence of some parameters resulting from the process

as specific surface area (SSA), morphology and impurities (Na₂O and SiO₂). Table 1 gives different characteristics of alumina powders used for this study.

The composition of the mixtures consists of 2/3 CA and 1/3 Al₂O₃, mixed in ethanol (50 wt%). This CA is before mixing, hydrated, then dehydrated to the powder becomes more reactive. So the chemical composition of CA is a mix of CaO, C₁₂A₇, CA, and γ-Al₂O₃. This slurry is then placed into a rotative jar mill using alumina balls as milling media during 24 hours. Some mixtures were also obtained by mixing boehmite (50 wt%), named (2+bo and 3+bo).

Table 1. Characteristics of alumina powders.

Al ₂ O ₃	1	2	3	4	2+bo	3+bo
SSA [m ² /g]	1.0	2.8	5.5	8.9	101	102

After drying, some parallelepiped pellets are shaped from mixed powders by uniaxial pressing at 350 MPa. After that, all samples were fired at 900, 1000, 1100 and 1260°C with a dwell time of six hours. Some hot-pressed samples have been made also using a hot press at 40 MPa and at 1000°C or 1100°C during a dwell time of six hours, in order to identify the effect of alumina impurities.

In order to characterise the influence of impurities, we used different aluminas in the same range of specific surface area but which are distinguished by their content of impurities. Their characteristics are presented in Table 2.

Table 2. Characteristics of alumina powders.

Al ₂ O ₃	A ₁	A ₂	A ₃
SSA [m ² /g]	7	8	8
Na ₂ O [ppm]	3000	500	500
SiO ₂ [ppm]	300	500	700

The comparison between alumina A₁ and A₂, which have a similar rate of silica, will allow to identify the influence of impurity Na₂O, and the comparison between alumina A₃ and A₂ will allow to see the influence of impurity SiO₂. Several techniques are used to characterize the materials. The phases are identified and quantified by the technique of X-Ray Diffraction. Microstructure observations were performed on a scanning electron microscope SEM (6500F JEOL).

3. Results and discussion

3.1. Influence of specific surface area on the reactivity of the system

Several phase transformations from CA or C₁₂A₇ and alumina occurred in the temperature range of 900-1300°C [1, 2]:
At 900°C: C₁₂A₇ + 5A → 12CA

The first reaction is accompanied by a volume shrinkage around 1 %.

At 1000°C: CA + A → CA₂

The second reaction is accompanied by a significant increase of volume around 13 %.

At 1300°C: CA₂ + 4A → CA₆

The last reaction, as the second one, is accompanied of a slight increase of volume. However the temperature of the reaction is not included in the temperature range of the study. Fig. 1 represents the molar percentage of CA₂ phase formed as a function of temperature.

The materials made from clinker CA and aluminas 1, 2, and 3 have the same content of CA₂ phase at 1000°C after

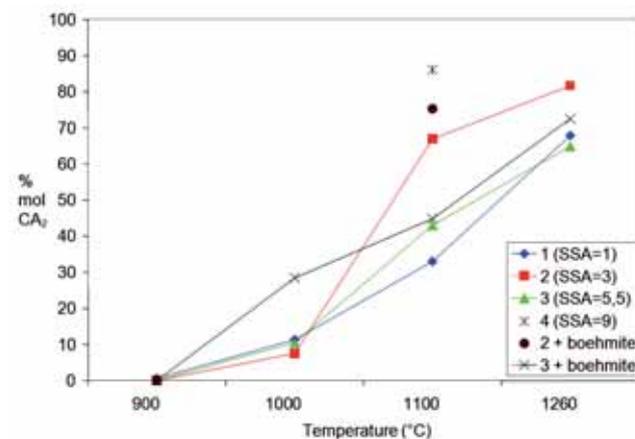


Fig. 1. Evolution of the molar amount of the CA₂ phase formed in materials made from clinker CA as a function of temperature of heat treatment (6 h).

six hours of dwell time, with the exception of the mixture of alumina 3+boehmite. This addition of boehmite allows faster phase formation as we will see later. However, at 1100°C after six hours of dwell time, alumina 2, which nevertheless has a specific surface lower than 3, is more reactive and the CA₂ content formed is more important. The reactivity of mixtures follows the order of the specific surfaces areas of alumina, with the exception of alumina 3 in relation to a dispersion problem. It was observed that this powder presents naturally many agglomerates, so it is difficult to attain homogeneous mixtures, despite the milling process. At 1100°C, we find that the addition of very fine powder of boehmite has a positive effect on the reactivity for both alumina 2 and 3 tested.

We can conclude that high specific surface area has a positive effect on the reactivity of the phases.

3.2. Effect of boehmite addition

Fig. 2 represents the molar percentage of the CA₂ phase formed as a function of temperature, for alumina 3 and the 3 + boehmite mix.

This figure shows that the boehmite reacts preferentially with the free lime of the system between 900 and 1000°C to form the CA phase, which formed the CA₂ phase from 1000°C. Once boehmite is totally consumed, alpha alumina reacts with calcium phases. The boehmite allows to form

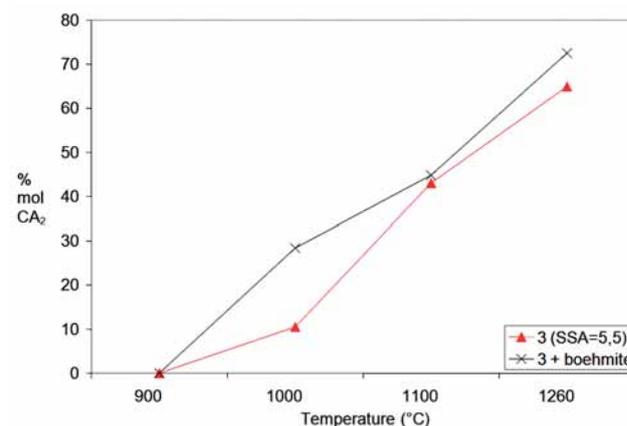


Fig. 2. Evolution of the molar amount of the CA₂ phase formed in materials made from clinker CA and alumina 3 and 3+boehmite as a function of temperature of heat treatment (6 h).

phases earlier in temperature and can therefore act as an accelerator of the reactivity at lower temperature.

3.3. Influence of alumina specific surface area on the microstructural evolution

The microstructures of materials of CA₁ and CA₃+boehmite are presented in Figs. 3 and 4. We showed that the specific surface area has an influence on the microstructure.

Based on these observations, regardless of the reactivity of alumina, at 1260°C the microstructure becomes vermicular type for all aluminas. The size of the alumina particles has an influence on the grain size of the microstructure and allows microstructures to become more or less homogeneous.

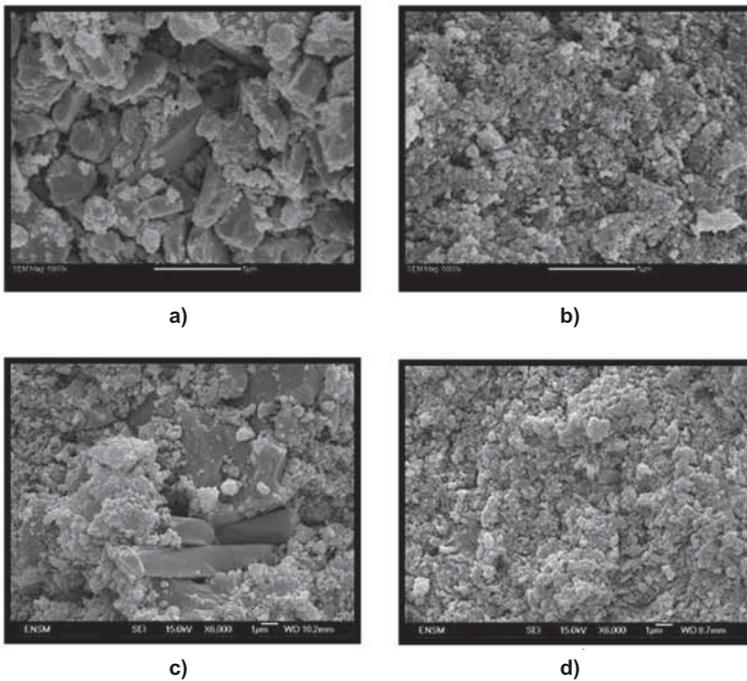


Fig. 3. Microstructures of materials CA_1 (a, c) and CA_3+boehmite (b, d), at 900°C, 1000°C (6 h).

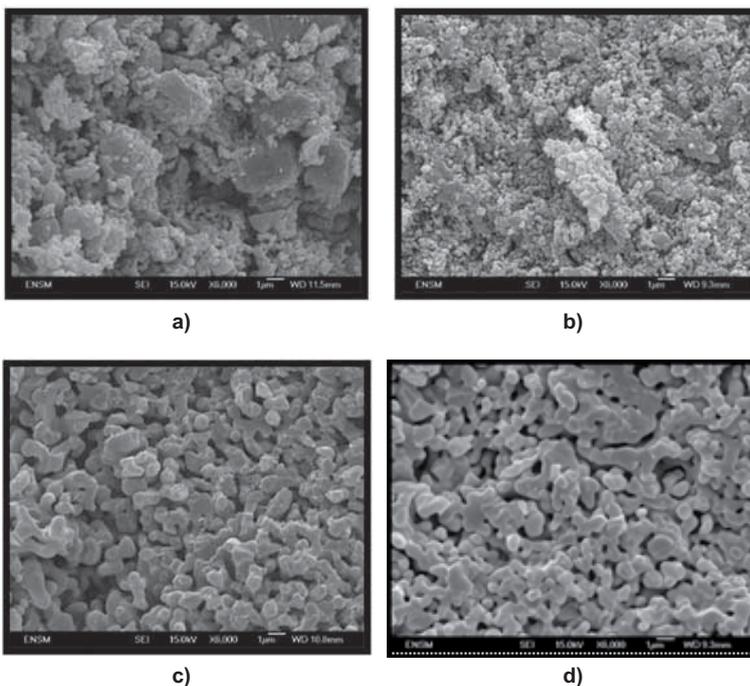


Fig. 4. Microstructures of materials CA_1 (a, c) and CA_3+boehmite (b, d), at 1100°C, 1260°C (6 h).

3.4. Influence of the morphology of alumina on the size and shape of calcium aluminates

In addition, a relationship between the morphology of the alumina and the calcic phase formed was highlighted. By comparing the microstructural observations of the sintered compact CA_1 treated at 1000 and 1100°C (Fig. 3c and Fig. 4a), we can see that the morphology of the CA₂ phase formed at 1100°C corresponds to the morphology of the starting alumina. Indeed, CA₂ aggregates formed at 1100°C have the same shape and same size as the starting

alumina, which leads to the hypothesis that these aggregates have some memory of the morphology of alumina.

The following figure (Fig. 5) shows the pattern of formation of phases from alumina and calcium aluminates of CA or C₁₂A₇.

We can assume that calcium ions Ca²⁺ diffuse towards alumina to form calcium aluminates [3, 4]. Small grains will germinate at the expense of the alumina and the aggregates of this new phase retain the memory of the alumina form [5, 6].

3.5. Influence of impurities on system reactivity

After identifying the influence of specific surface area of alumina on the reactivity of the system, we studied the influence of impurities of alumina on the reactivity of the phases. The study occurred with a series of aluminas, in the same range of specific surface area (7-8 m²/g) but with different impurities contents studied here are the silica and sodium oxide. We can find in the literature some information about the influence of these impurities on the microstructure of sintered alumina [7, 8], but poor information on the influence of these impurities on the phase transformations or calcium diffusion coefficients in calcium aluminates. Fig. 6 presents the aluminas used for this study among their content of Na₂O and SiO₂.

Fig. 7 represents the phase CA₂ formation of materials made from CA powder (CA > 99 %) and alumina A₁, A₂ and A₃.

This calcium aluminate CA, because it is not ground in the same way as the first one, presents CA coarse aggregates and is therefore not very active. By comparing the reactivity of these materials, we find the following order of reactivity: A₃ > A₁ > A₂. We put forward a positive influence of impurities SiO₂ and Na₂O, with a marked effect of SiO₂.

To confirm these results and compare the kinetics of reaction of each mixture, diffusion couples were carried out in the hot press, and characterized by establishing the concentration profiles in EDX analysis. In fact, three diffusion

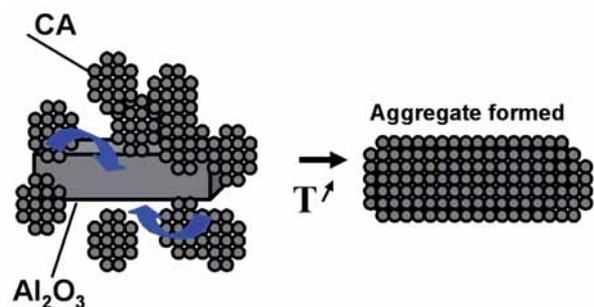


Fig. 5. Schematic illustration of the formation of aggregates of calcium aluminates by consumption of alumina.

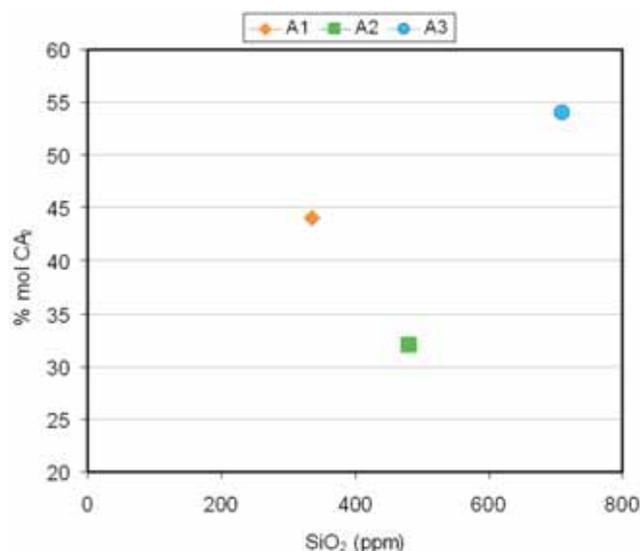


Fig. 6. Classification of alumina according to their content of Na_2O and SiO_2 .

couples were carried out with alumina A_1 , A_2 , and A_3 , and pure calcium aluminate CA (over 99 %). In a graphite matrix, a layer of powdered CA is filed, followed by a layer of alumina. Each diffusion couple has the same thermal cycle (1100°C), with two different dwell times, two hours and six hours, and a uniaxial pressure of 40 MPa to maintain contact and optimize the reaction between the two constituents.

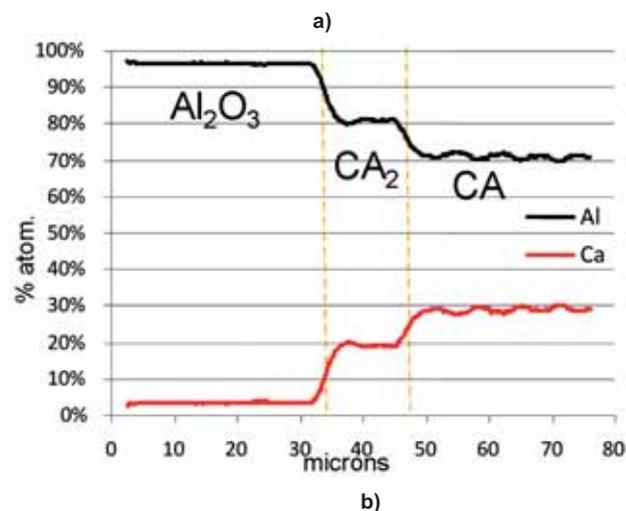
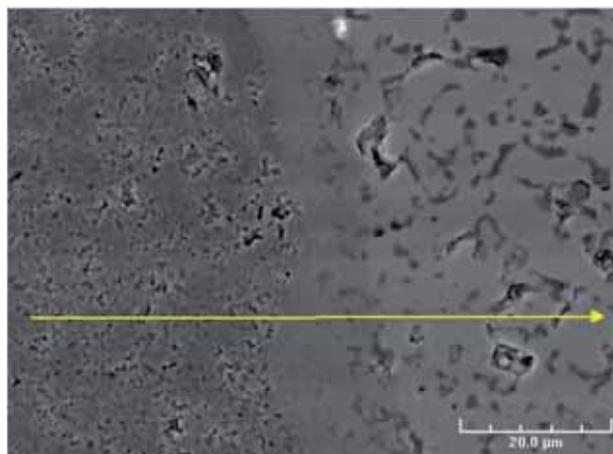


Fig. 8. Diffusion couples CA_3 , $1100^\circ\text{C}_6\text{h}$.

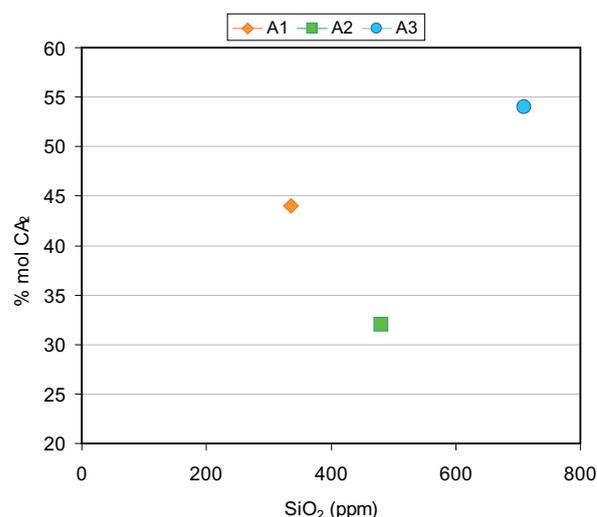


Fig. 7. Formation of the CA_2 phase in materials made from CA and aluminas A_1 , A_2 , and A_3 .

On the sintered samples, a section was made, on which a diffusion profile was measured using the EDX analysis.

Fig. 8a represents images taken with a scanning electron microscope (back scattering mode) and in Fig. 8b the percentage of atomic elements calcium and alumina is represented, depending on the analyzed thickness in microns, for the diffusion couple with alumina A_3 .

For the material sintered at 1100°C for a dwell time of 2 hours, the average of thickness of reaction at the interface is about 6 microns, and for a dwell time of six hours, it is about 10 microns.

Table 3 represents the thickness of zone reaction of the interface CA-aluminas A_1 , A_2 , and A_3 .

These results confirm those of the preceding paragraph, in fact the most important reactivity is obtained for alumina with high content of impurities in silica and sodium oxide. We can therefore say that the silica and sodium oxide have a positive influence on the reactivity of the system, with a greater effect of the silica.

To confirm this effect of silica, we carried out two diffusion couples with a Baikowski alumina SM8 and a mix with SM8 and addition of silica gel. This gel has been incorporated in SM8 alumina slurry in alcohol (content of 700 ppm), and was mixed overnight in the roller mixer. The mixture then underwent a thermal cycle of more than 20h at 600°C , to distribute silica in the alumina. The thermal cycle is the same as above 1100°C for 6 hours. The thicknesses of reaction zones at the interface were compared. Table 4 presents the measured thicknesses.

The thickness measured for the couple without silica gel is about 5 microns, while that for the couple with silica gel is about 9 microns.

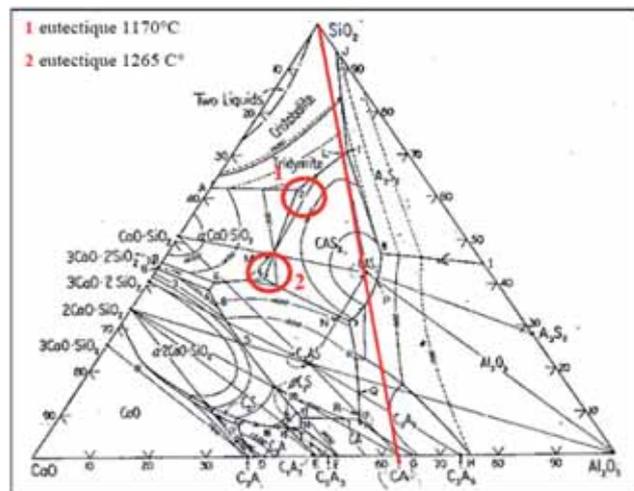
We can therefore say that silica allows a better reactivity of the system, leading to the CA_2 formation.

Table 3. Thickness of reaction zones at the interface alumina – CA.

Aluminas	A_1	A_2	A_3
Average thickness ($1100^\circ\text{C}_2\text{h}$) [μm]	$5 \pm 0,5$	$3 \pm 0,2$	$6 \pm 0,8$
Average thickness ($1100^\circ\text{C}_6\text{h}$) [μm]	$9 \pm 0,5$	$6 \pm 0,2$	$10 \pm 0,8$

Table 4. Thickness of reaction zones at the interface alumina – CA.

Aluminas	SM8	SM8+silica
Average thickness (1100°C_6h) [μm]	5 ± 0,5	9 ± 0,3

Fig. 9. Ternary diagram CaO-Al₂O₃-SiO₂.

In some cases, sintering said “solid phase”, the presence of impurities can lead to the formation of a liquid phase confined at grain boundaries, which can help the diffusion of species. These secondary phases are generally characterized by low eutectic melting temperature. We found, in the system CaO-Al₂O₃-Na₂O, and in the system CaO-Al₂O₃-SiO₂, that liquid phases could be formed at the temperatures studied (800-1200°C). We can attribute the positive effect of impurities on the diffusion of calcium stimulated by a liquid phase at interfaces. The ternary phase diagram CaO-Al₂O₃-SiO₂ reveals the presence of ternary eutectic whose temperature is equal to 1170°C and 1265°C (Fig. 9).

The diagram presented in Fig. 10, shows that for compositions between the sodium disilicate (Na₂O·2SiO₂) and albite (Na₂O·Al₂O₃·6SiO₂) and between sodium disilicate and nepheline (Na₂O·Al₂O₃·2SiO₂), can be respectively eutectic points at 767°C and 768°C. These formations of liquid phases could explain a better diffusion of calcium species, and thus a better reactivity of the system. In fact, the sintering of our compound here is a “solid phase” sintering, that is all the components remain solid at the temperature of heat treatment. We know that in some cases, the presence of impurities can lead to a liquid phase confined to interfaces between two components, and therefore it can help the diffusion species.

4. Conclusions

This study has allowed the authors to describe the interaction between the parameters of alumina and the parameters of microstructure of materials models made from alumina and calcium aluminates CA.

It also allowed them to highlight the parameters of the alumina which have an influence on the parameters of microstructure, the evolution of the calcium phases in temperature, morphology, and size of grains. In the first step, we have seen that the specific surface of alumina has a significant influence on the reactivity of the system, with the exception of alumina poorly dispersed. Indeed, we have seen that according to the alumina used, the reaction paths were different. Moreover, the addition of fine alumina, transition alumina, can change the temperature of the reaction phases, and therefore can act as an accelerator of phase formation.

Alumina can also provide final microstructures of materials finer and homogeneous, these microstructures are all type vermicular at 1260°C. This study has shown that the mode of formation of calcium phases is by diffusion of Ca²⁺ from calcium-rich phases to the alumina or to alumina-rich calcium aluminates. Therefore, alumina imposes the morphology of calcium phases aggregates formed. As the alumina is fine, so the microstructure of the phases formed at higher temperatures will be fine.

In addition to the specific surface area and morphology of alumina that have an influence on reactivity, there is also an influence of these impurities on the reactivity. Alumina with high content of silica and sodium oxide promote greater reactivity of the phases. The study of ternary systems CaO-Al₂O₃-Na₂O and Al₂O₃-Na₂O-SiO₂ guides us to the assumption that the liquid phases can be formed at the interface between the reactants and promote the diffusion of calcium species into alumina. These liquid phases have low melting points that correspond to the temperature range of this study.

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