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Mechanism of pore generation in calcium hexaluminate (CA_6) ceramics formed *in situ* from calcined alumina and calcium carbonate aggregates

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ABSTRACT

Porous structures of calcium hexaluminate ($CaAl_{12}O_{19}$ or CA_6) are resistant to densification, chemical attack and thermal shock and have been widely employed in thermal insulators for high temperatures (above 1400 °C). Despite its technological importance, little is known corcerning the *in situ* formation of CA_6 from the early calcination temperatures (500–900 °C) up to full sintering (above 1000 °C). This study investigated the mechanisms of pores generation in *in situ* CA_6 obtained from a mixture of calcined alumina (α-Al_2O_3) and chemically precipitated calcium carbonate ($CaCO_3$) aggregates. The evolution of the microstructure was followed by scanning electron microscopy, X-ray diffraction, dilatometric analysis, and measurements of physical properties, in the 500–1500 °C temperature range. Samples of 50-40% total porosity and different degrees of linear expansion were obtained after sintering at 1100–1500 °C, respectively. The crystallization of liquid phases of eutectic composition played a major role in the formation and maintenance of pores after $CaCO_3$ decomposition.

1. Introduction

1.1. *General aspects of the CaO-Al_2O_3 system*

The CaO-Al_2O_3 system (or C-A) is an important input for the production of two refractory materials, namely calcium aluminate cements (CACs) and calcium hexaluminate ($CaAl_{12}O_{19}$, $CaO{\cdot}6Al_2O_3$ or CA_6) [1–4]. CACs are produced by solid-state reactions between CaO and Al_2O_3 sources (typical examples are calcium carbonate and lime and bauxite or calcined alumina, respectively) that create a mixture of different calcium aluminates (mainly C_3A, $C_{12}A_7$ and CA) [5–7]. Initially, the several possible precursor raw materials decompose during the first stages of heating (from 250 °C up to 750 °C), which results in a combination of Al_2O_3 and CaO, according to the general expressions

$$2Al(OH)_3 \xrightarrow[250-350^{\circ}C]{} Al_2O_3 + 3H_2O_{(Gas)} \tag{1}$$

$$Ca(OH)_2 \xrightarrow[420-580^{\circ}C]{} CaO + H_2O_{(Gas)} \tag{2}$$

$$CaCO_3 \xrightarrow[590-753^{\circ}C]{} CaO + CO_{2(Gas)} \tag{3}$$

As the heating proceeds, the compounds formed at around 1362 °C are usually a mixture of C_3A, $C_{12}A_7$, and CA, which are the phases of lowest melting point in the system (Fig. 1). The control of the CaO-Al_2O_3 ratio in the initial composition of the mixture and the heating-cooling rates enables other phases, as CA_2, to be formed along the reaction time [3,4,6,7]. After milling for granulometric adjustments, such calcium aluminates behave as hydraulic binders in castables and mortars for many refractory systems and variations in their proportion enable the design of cements of different setting times [4,7].

Differently from other calcium aluminates, CA_6 does not react with water and, therefore, is not suitable for cement production. On the other hand, over the two past decades, it has became one of the most important raw materials for refractories because of its unique combination of resistance to slag corrosion, thermal shock, and creep [8–12]. The next sections briefly address such developments.

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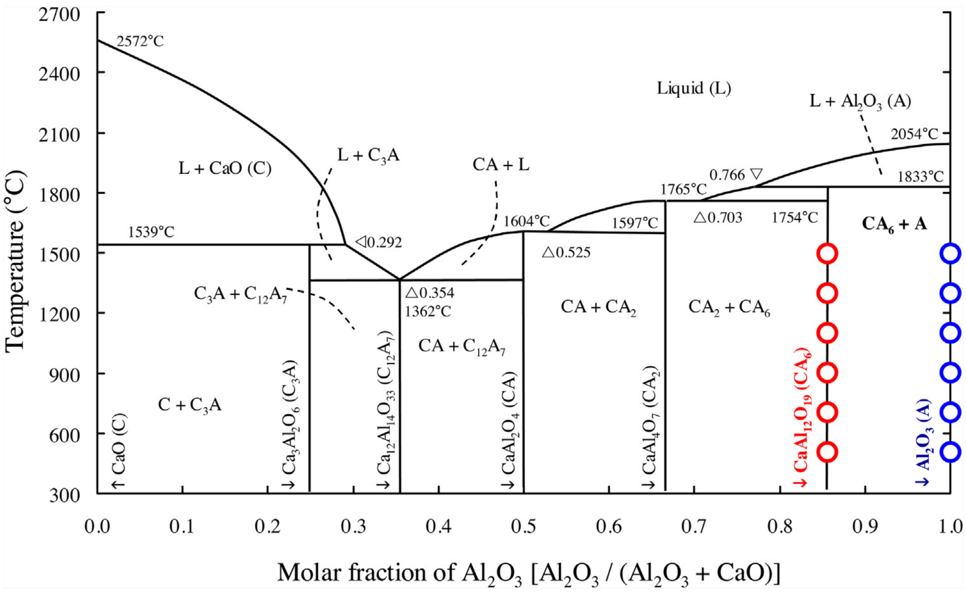

Fig. 1. Phase diagram of the CaO-Al_2O_3 system (adapted from [1,6]). Circles on the right side indicate the compositions and thermal treatment temperatures tested.

1.2. Routes for the obtaining of calcium hexaluminate

CA_6 is obtained by high-temperature reactions (above 1300 °C) amongst sources of Al_2O_3 (for instance, calcined [1,6,13–17] and tabular alumina [8–12], hydratable alumina (ρ-Al_2O_3, [16,17]), boehmite (AlOOH, [18]), $Al(NO_3)_3$ [19–22] and $Al_2(SO_4)_3$ [23]) and CaO ($CaCO_3$ [1,13–17], $Ca(OH)_2$ [16], CaO from dead-burnt $CaCO_3$ [6,16,24] and calcium aluminate cement [25–29]) and different processing routes (solid-state reaction amongst compacted raw materials [3,8–17], liquid-phase assisted sintering [1,20], sol-gel synthesis [18], and soluble salt co-precipitation [19–23]). For a general view of this solid-state reaction, let us assume a perfectly dispersed agglomerate-free and random mixture of thin CaO and Al_2O_3 particles (or their precursors) combined to produce a CaO:Al_2O_3 molar ratio of 1:6. In this configuration, CaO particles are most likely surrounded by Al_2O_3 ones. The reaction begins at around 1000–1100 °C with the interdifusion of Ca^{2+}, Al^{3+} and O^{2-} ions preferentially at the contact points amongst particles. Ca^{2+} ions are diffused more rapidly into Al_2O_3 than Al^{3+} in CaO, so that the electrical neutrality of the system is kept [1,2,6,14,24,30–33]. At these contact spots and after a certain reaction time, the CaO-Al_2O_3 ratio can be significantly different from the total composition of the system, therefore, low melting temperature compounds (C_3A, $C_{12}A_7$ and CA) begin to form around 1360 °C, according to the expressions:

$$CaO + 6Al_2O_3 \rightarrow (1/3)Ca_3Al_2O_6 + (17/3)Al_2O_3 \quad (4)$$

$$(1/3)Ca_3Al_2O_6 + (17/3)Al_2O_3 \rightarrow (1/12)Ca_{12}Al_{14}O_{33} + (130/12)Al_2O_3 \quad (5)$$

$$(1/12)Ca_{12}Al_{14}O_{33} + (130/12)Al_2O_3 \rightarrow CaAl_2O_4 + 5Al_2O_3 \quad (6)$$

Above 1360 °C, as the molten calcium-rich aluminates dissolve the nearest Al_2O_3 particles, the Al^{3+} concentration in the liquid increases and forms CA_2:

$$CaAl_2O_4 + 5Al_2O_3 \rightarrow CaAl_4O_7 + 4Al_2O_3 \quad (7)$$

As CA_2 has a higher melting point than $C_{12}A_7$ and CA, at 1400–1500 °C temperature ranges, the liquid phase begins to crystallize in platelet grains [6,14,31,32]. After this point, no significant liquid phase is present in the system and the reaction continues as a slower solid-state diffusion process up to the total consumption of Al_2O_3 and formation of CA_6:

$$CaAl_4O_7 + 4Al_2O_3 \rightarrow CaAl_{12}O_{19} \quad (8)$$

The solid-state reactions that form CA_6 and CA_6-Al_2O_3 composites depend fundamentally on the contact points amongst the reactant particles. Therefore, they are affected mainly by four parameters, namely type of CaO and Al_2O_3 sources, degree of proximity of the particles, average size ratio, and presence of impurities or other compounds (particularly, MgO, SiO_2 and Fe_2O_3) [14,34–36].

Reactions between non-oxide precursors, such as $CaCO_3$, $Ca(OH)_2$ and $Al(OH)_3$ usually produce highly asymmetric platelet CA_6 grains after an intense crystal growth along the basal plane of the structure. Such a morphology preserves a significant level of inter-grain porosity. On the other hand, the combination of stabilized oxide precursors (particles of dead-burnt CaO and of α-Al_2O_3) generates a homogenous microstructure of equiaxial grains and high levels of relative density [13,14,31,34]. Despite the lack of deeper investigations on the early stages of those reactions (between 1100 and 1500 °C), previous studies suggested such differences in the resulting microstructure can be attributed to the average distance amongst the reactant particles. When particles of carbonates and hydroxides are thermally decomposed, they undergo a volumetric shrinkage and density increase due to the release of CO_2 and water, respectively [37–42]. Therefore, part of the space originally occupied by those particles in the compact becomes empty, which generates significant levels of inter-particle porosity. In a combination of $CaCO_3$ and α-Al_2O_3, for instance, the $CaCO_3$ decomposition increases the average inter-particle distance and reduces the number of effective contact points amongst the reactants. Because solid-state diffusion must occur through a reduced number of contact points, such regions tend to form asymmetrical CA_6 crystals. Conversely, the mixing of CaO and α-Al_2O_3 produces no volumetric shrinkage and a large number of effective contact points behave as diffusion paths that generate more equiaxial grains.

Imperfect contact points amongst Al_2O_3 and CaO particles also appear when the precursors have largely different average parti-

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