

Production and Properties of Refractory Raw Materials Based on Andalusite and Mullite – Influence of Impurities in the Refractory Behavior

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Mullite based refractories represent one of the main groups of acid refractories. Their outstanding thermo-mechanical properties and stability make them key components of many refractory solutions.

This paper describes the main properties of andalusite and mullite based products, and investigates the impact of mineral purity in the enhancement of their performance in the refractory applications.

Mullite and andalusite – mineral structure and mullitization

Most of the acid refractory materials can be described on the system $Al_2O_3 - SiO_2$ (Fig. 1). This system is characterized by three phases: silica, mullite and corundum. They are thermodynamically stable at high temperature with a congruent melting point at respectively 1726, 1853 and 2054 °C respectively [1]. Due to the high liquidus temperature and the high temperature of the eutectic (1595 °C), aluminosilicates are generally considered as having good refractory properties, although their performance can be significantly affected by impurities. In particular alkali, alkali-earth oxides or even iron oxides can be responsible of a significant drop of the refractory behavior, to the point that the impurity content is often considered as more critical than alumina in the determination of the refractory behavior.

Mullite, which is a mineral existing under the form of $3Al_2O_3 \cdot 2SiO_2$ or $2Al_2O_3 \cdot SiO_2$, provides attractive properties for refractory

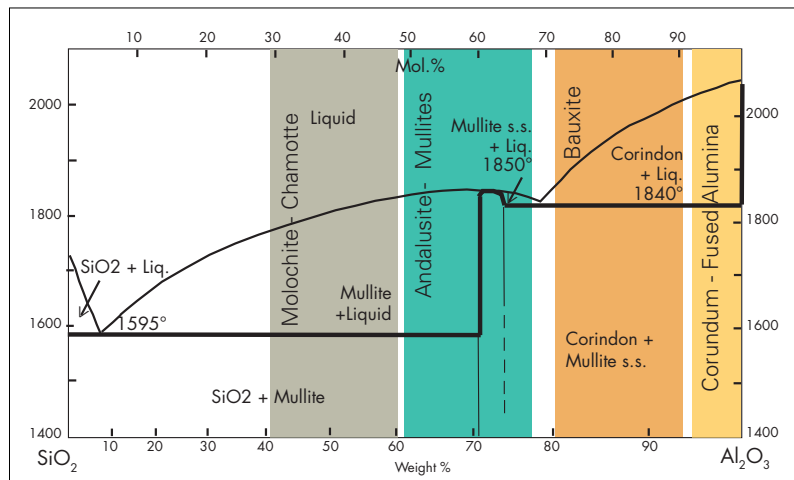


Fig. 1 This diagram reflects the behavior of pure materials without taking into account the impact of impurities

systems (low thermal expansion, low thermal conductivity, good chemical stability, excellent thermo-mechanical stability). Unfortunately, mullite rarely occurs as natural raw material. Consequently, the development of mullite in commercial refractory has to be achieved by firing various aluminosilicates, with suitable chemical composition, involving clays, kaolin and various fine silica and alumina products.

Among the aluminosilicate raw materials, andalusite is the best natural source of mullite and can be beneficiated in order to achieve a very high degree of purity, as it is available in sizes up to 8 mm.

Andalusite transforms into mullite at relative low temperature, with a minor volume expansion (+4,5 %). For this reason, andalusite in refractory products can be used as fired (fired bricks) or unfired (unfired bricks, castables, plastic mixes) therefore taking advantage of the expansion resulting from the mullitization stage.

Unlike most of the other aluminosilicates, the mullitization of andalusite does not involve any dehydration stage consequently does not generate intrinsic porosity. For

this reason, refractory materials based on andalusite, either raw or calcined, exhibit porosity significantly lower than bauxite or chamotte. When applied in castables, this specific behavior of andalusite results in an improved corrosion resistance as well as a lower water demand.

The process and the kinetic of mullitisation have been studied by several authors and is fully described in related literature [2]. Several works [3] investigated the impact of impurities on the process and demonstrated a direct correlation between the mullitization rate and the purity of the starting andalusite mineral. The lower the amount of impurity, the higher the amount of mullite achieved during firing.

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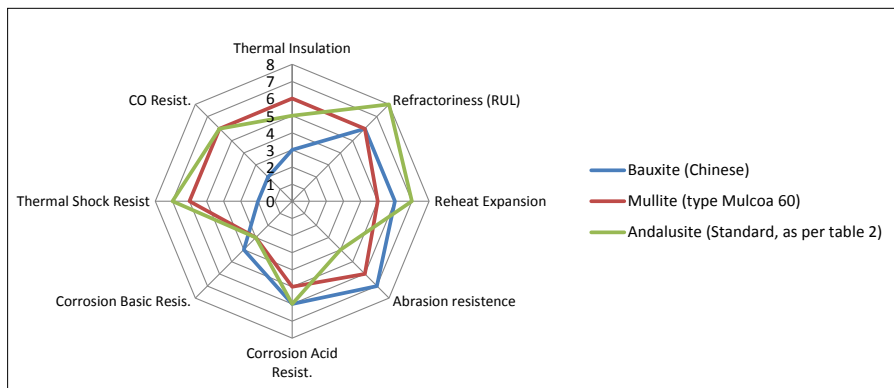


Fig. 2 Qualitative description of the performance of three classes of refractories (graduation from 9 to 8, 1 being the lowest performance)

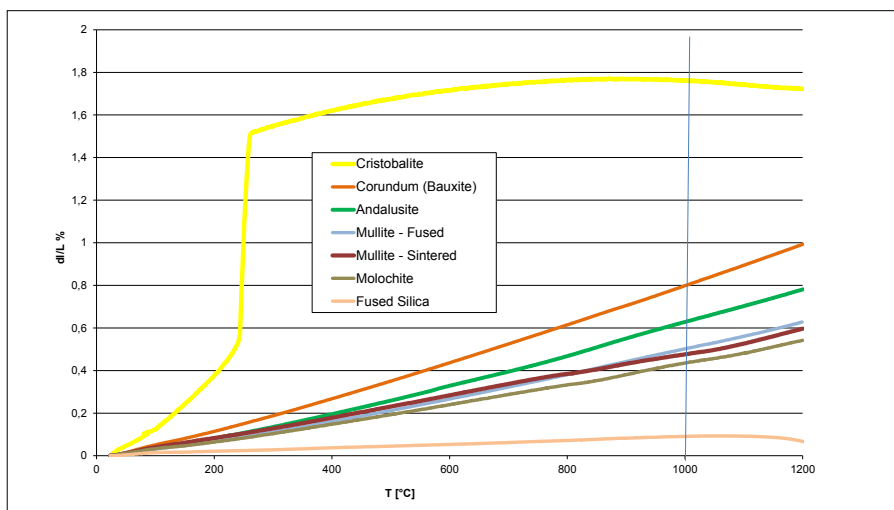


Fig. 3 Thermal expansion diagramme

Refractory properties and performance

Given the high alumina content, the performance of andalusite based products is often compared to mullite and bauxite. The chart (Fig. 2) provides a qualitative description of the performance of these three classes of refractories which are based on the properties commonly considered as critical in the modern refractory industry.

Despite the similar alumina content, there are notable differences on the performance. Corrosion and abrasion resistance are likely the key properties that characterize the performance of bauxite and makes this material suitable for applications where the refractory lining is subject to strong mechanical and chemical stresses.

On the other hand, due to the high content of free iron, CO resistance is often considered as a weak point of bauxite. Therefore the use of this material in applications such as hot

blast stoves in iron making or anode baking furnace for the aluminum industry, where the exposition to CO at low temperature is a major requirement is not recommended.

Thermal expansion and thermal shock resistance

Thermal Shock Resistance (TSR), and more generally any property related to the thermo-mechanical stability, are traditionally considered as one of the most important features of mullite and mullite based materials.

This can be partially explained by the low and linear coefficient of thermal expansion (CTE) that is typical of any mullite based material ($\alpha = 4,5-6,5 \cdot 10^{-6}K^{-1}$), whereas corundum based materials, such as bauxite, BFA, WFA or tabular alumina, shows a CTE in the area above $8 \cdot 10^{-6}K^{-1}$. The chart (Fig. 3) illustrates the thermal expansion diagram of several materials.

Andalusite has an average thermal expansion of 0,6–0,7 % in the range 0–1000 °C,

which slightly decreases once the andalusite is completely transformed into mullite. Among the other materials, fused silica shows by far the lowest thermal expansion. This is a material entirely constituted of amorphous silica and represents the behavior that can be expected from any glassy phase with a high degree of purity. Unfortunately, the use of this material is limited to applications where the refractory is not subject to thermal cycling from high temperature (above 1000 °C) to room temperature, due to the devitrification process that occurs above 1000 °C. By contrast, materials that associate the benefits of mullite and amorphous phase to optimize the thermal shock resistance exist. This is the case of Molochite, which is a composite material made of mullite (roughly 55 %) and amorphous phase (45 %), with a specific production process that prevents the formation of cristobalite. This material is therefore largely used in applications requiring low thermal expansion and high thermal shock resistance, such as ceramic kiln furniture.

Several models have been developed in the last decades to predict the thermal shock resistance behavior of different materials of intrinsic properties. The traditional model, based on the thermo elastic theory [4], establishes a correlation between the TSR and several material properties, such as the coefficient of thermal expansion (CTE), the young modulus and the thermal conductivity.

Recent studies [5], however, have highlighted the impact of the composite structure of the material on the TSR, with particular attention to the micro cracking network resulting from a mismatch of CTE between the different phases or different orientations of the crystal.

The anisotropic character of andalusite crystal (orthorhombic) leads to three different CTE values along the three axis of the crystal (Fig. 4).

Thus, differences in CTE values between andalusite aggregates and matrix can here induce either debonding at the interface or radial micro cracks of the matrix around the aggregates (Fig. 5). This has been recognized as one of the main reasons for the outstanding thermal shock resistance of andalusite based refractory products.

Refractoriness under load

The hot behavior of a refractory material is strongly dependent on the mineralogical

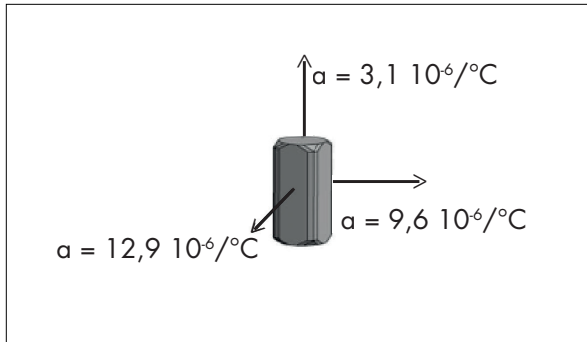


Fig. 4 The anisotropic behavior of andalusite crystal, which shows a different coefficient of thermal expansion for each of the crystallographic axis

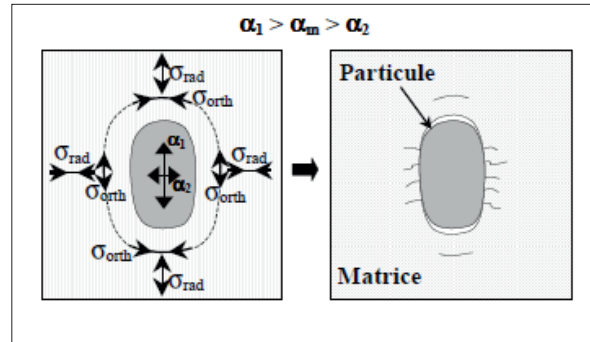


Fig. 5 Modeling of the micro-cracking formation on the boundary of an andalusite crystal (Krakroudi [5])

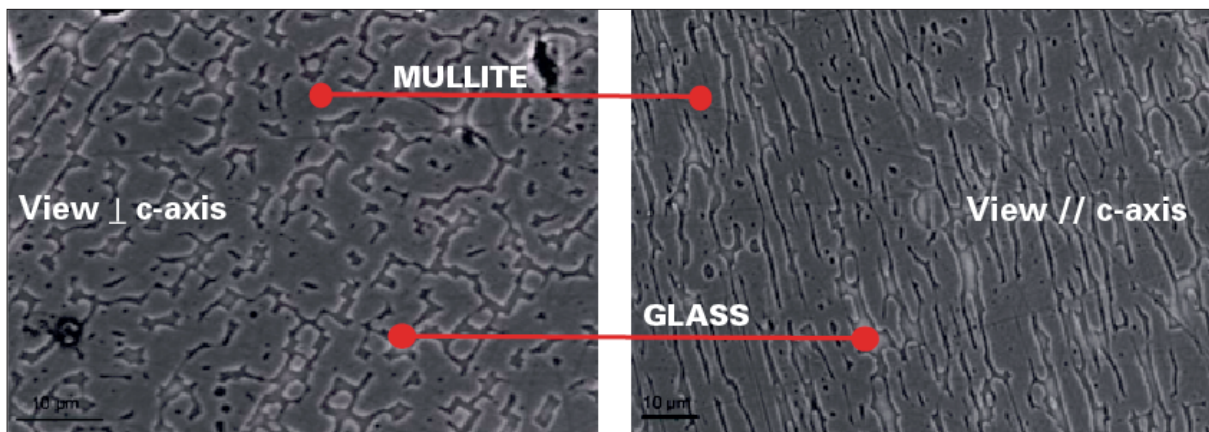


Fig. 6 Microstructure of mullitized andalusite

composition. In particular, the amount and the nature of the amorphous phase plays an important role on properties such as the refractoriness under load and creep resistance. As already discussed, the presence of impurities contributes significantly to the formation of amorphous phase [6].

Furthermore, the viscosity of this amorphous phase is severely decreased by the presence of impurities, in particular alkalis, such as K_2O and Na_2O , and is thus responsible for lowering the softening point of the material.

It becomes obvious that the deformation of the hot material under load will be strongly decreased by a reduction of the amount of impurities, particularly when the impurities are concentrated in the matrix of the refractory products.

Due to a low amount and high viscosity of the liquid phase and a very rigid structure of the mullite network, andalusite refractories show a very high refractoriness under load. This result cannot be obtained with other aggregates of similar alumina content (Fig. 6).

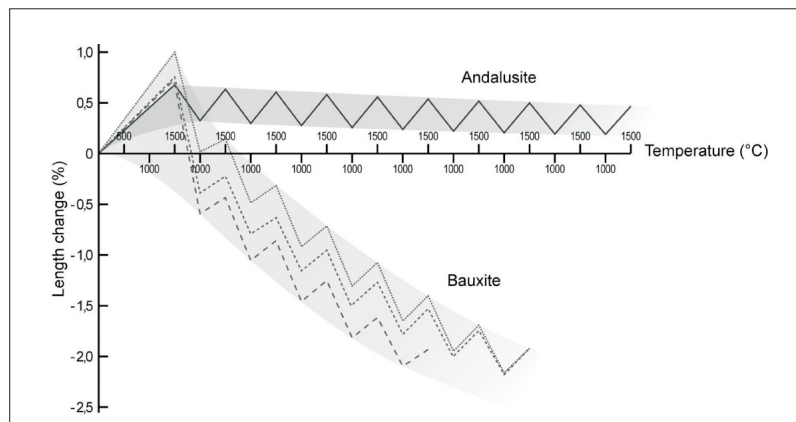


Fig. 7 Creep of andalusite and bauxite bricks: temperature change between 1000 –1500 °C; load: 0,2 N/m², property determined by Buhr und Koltermann

As demonstrated in several previous works [7], andalusite refractories show also a very high creep resistance during thermo-cycling between 1000 – 1500 °C. (Fig. 7). This property is a significant advantage of andalusite based bricks versus bauxite, which is particularly relevant for any application requiring thermal cycling at very high temperature.

Applications

Andalusite and mullite can be used as main constituents or additives in the refractory lining of liquid iron and steel vessels [8-10] as well as many other applications in glass, cement, petro chemistry, incinerations and aluminum (Tab. 1). Their application has

Tab. 1 Applications of andalusite and mullite

Industry	Critical Properties	Application
Iron making	CO resistance, thermal shock resistance, creep resistance	hot blast stove
		blast furnace and runners
		torpedo ladles
		iron ladle
Steel making	thermal shock resistance, corrosion resistance	steel ladle (working and safety lining)
		tundish
		re-heating furnaces
Aluminium	creep resistance	anode baking furnaces
Glass	purity, alkali resistance, freedom from contamination	regenerators
		feeders
		glass tank
Cement	alkali resistance, thermal shock resistance	pre-calcination
		rotary kiln
		cooling area
Ceramic	refractoriness under load, thermal shock resistance	kiln walls and roof
		kiln cars
		kiln furnitures and rollers
Incinerators	corrosion resistance, thermal shock resistance	fluidized bed, rotary furnace

Tab. 2 Chemical composition [mass-%]

	Al ₂ O ₃ [%]	Fe ₂ O ₃ [%]	K ₂ O+Na ₂ O [%]	TiO ₂ + CaO+MgO [%]
Kerphalite KF	60,8	0,45	0,25	0,30
Durandal D60	60,8	0,42	0,20	0,25
Randalusite Premium	60,5	0,62	0,20	0,30
Standard Andalusite	59,3	0,72	0,32	0,38

become widely accepted not only in Europe but also in Asia and the Americas generating a significant decrease of the refractory consumption per tonne of steel across the world.

Present and future

Over the last decades, the most stringent requirements of the refractory users have pushed the raw material producers to work on the development of new grades, capable to further increase the performance of the refractory solutions.

New grades of andalusite have been developed in order to maximize the amount of mullite achievable after firing, reinforcing the matrix of bricks and castables and in return enhancing hot properties as well as corrosion resistance.

The amount of impurities (Na₂O + K₂O + CaO + MgO + Fe₂O₃ + TiO₂) has been re-

duced as much as 0,9 %, which represents a degree of purity unmatched in any other natural alumino-silicate. This is achieved through a complex sequence of purification stages involving heavy media separation, electrostatic separation and floatation (Tab. 2)

The behaviour of the refractory materials produced with high purity raw materials allows a substantial enhancement of hot performance. The maximum operating temperature now being significantly increased, open the door to new applications that were not addressable with standard andalusite and mullite grades before.

Imerys Refractory Minerals, in collaboration with the CARRD – the Imerys R&D Center for Refractory and Abrasive – is running several projects aiming to design and develop an appropriate selection of grades for specific applications. It may be said that investi-

gations are currently in progress on several critical applications, such as the working lining in the wall of steel ladles where the new grades of andalusite are expected to provide a substantial contribution to the enhancement of the performance under severe working conditions of the modern steel secondary metallurgies.

Furthermore, the author believes that the availability of higher purity grades as well as a more accurate understanding of their properties and performance will open the door to the formulation of composite solutions and optimized the outcome of technical synergies across the full range of minerals.

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