Effect of Al₂O₃ Particle Size on Mullite Formation by *In-Situ* Reaction of Aluminosilicate Castables

A Guo, Y B Xiang, S X Zhao, Y C Si, Q Gu*, Z M Wang*

State Key Laboratory of Advanced Refractories, Sinosteel Luoyang Institute of Refractories Research Co., Ltd., Luoyang 471039, Henan, China

Corresponding author: wangzm@lirrc.com

Abstract: The total output of unshaped refractories has been increasing in recent years due to its short production cycle, safety and energy saving, good integrity and so on. Among them, aluminosilicate castables have been widely used. In order to improve the high temperature properties of castable, Al₂O₃ micro powder and SiO₂ micro powder are usually used. However, few researchers have reported the effect of particle size in matrix on in-situ formation of mullite. In this paper, a mass dissolution rate model and a solution nucleation shrinkage model are established based on the control of the rate of in-situ mullite formation, which takes place by the dissolution of Al₂O₃ to the liquid phase formed by melting of SiO₂ powder containing impurities at high temperature. The results show that with the increase of Al₂O₃ particle size, the mass dissolution rate of independent particles was accelerated, and the nuclear shrinkage rate of Al₂O₃ particles decreased fastest when the particle size is 1-10μm. The dissolution rate increases with the increase of service temperature. Moreover, the complete dissolution time is shortened with the decrease of particle size of Al₂O₃. When the particle size is 80μm, it takes 100.31 seconds for a single particle to dissolve completely, but only 1.00 second when the particle size of Al₂O₃ decreases to 8μm.

1. Introduction

In order to improve the high temperature performance of amorphous refractories and respond to the call of national energy saving and emission reduction, the bonding system of amorphous refractories must be purified, however the calcium aluminate cement or CaO containing raw materials are negative to the high temperature properties and service life of aluminosilic refractories, which requires that the amount of calcium aluminate cement should be limited [1,2]. As far as aluminum siliceous castable is concerned, the in-situ formation of mullite and with mullite as combination in the matrix shows high fire resistance, good thermal stability and strength [3]. Therefore, the study of the influencing factors of in-situ mullite formation in aluminosiliceous castable plays an important role in improving the performance of refractories.

In order to reduce the amount of calcium aluminate cement in aluminosiliceous castable, silicon(SiO₂) powder and alumina(Al₂O₃) powder were mostly added to the fine powder. The small particle size of SiO₂ powder has a good filling effect on the gap formed between the particles in low cement castable, the formation of three-dimensional spatial network structure at medium and high temperature can improve the strength of castable, the most important thing is that SiO₂ powder is easy to form secondary mullite with Al₂O₃ in refractory raw materials at medium and high temperature, which can improve the strength of low cement castable after burning at medium and high temperature, and the formation of secondary mullite can also significantly enhance the thermal shock resistance [4-
When the content of SiO$_2$ powder reaches a certain extent, the enhancement effect on castable tends to be smooth, and the addition of high activity Al$_2$O$_3$ powder is more beneficial to the formation of mullite, thus greatly improving the strength of castable [8]. Silica micro-powder and activated Al$_2$O$_3$ micro-powder are the most commonly used aluminosilicate castable. At this stage, many scholars have added Al$_2$O$_3$ and SiO$_2$ to the fine powder of aluminosilicate castable to form mullite in situ at high temperature to improve its performance [9-15].

The in-situ formation of mullite by SiO$_2$ and Al$_2$O$_3$ in the matrix environment of aluminosiliceous castable belongs to the dissolution-precipitation mechanism, SiO$_2$ powder first forms liquid phase rich in SiO$_2$ under the action of a small amount of impurity oxides, substances containing Al$_2$O$_3$ in castable (including brown corundum, special bauxite and Al$_2$O$_3$ powder) dissolve in liquid phase, when the concentration of Al$_2$O$_3$ in SiO$_2$ phase exceeds the critical concentration (cnc), reaches saturation, mullite crystals begin to precipitate, mullite begins to nucleate and grow [16,17]. B. Saruhan [18] found that the formation of mullite could be observed by amorphous SiO$_2$ and Al$_2$O$_3$ below 1500°C. This formation mechanism involves three rate processes [19]: (1) The dissolution process of Al$_2$O$_3$ particles into amorphous SiO$_2$-rich matrix phase. (2) The diffusion process of Al$_2$O$_3$ to the grown mullite grains. (3) The process of combining Al$_2$O$_3$ with mullite surface into mullite crystal lattice. The rate of in situ formation of mullite is controlled by the dissolution rate of transition Al$_2$O$_3$ particles in amorphous phase at low temperature($\leq 1650^\circ$C), at high temperature, it is controlled by diffusion rate [20]. There may be three rate control mechanisms for the dissolution process at low temperature, the first is the dissolution mechanism of the reaction control, the second is the dissolution mechanism of mass transfer control, the third is the dissolution mechanism of the heat transfer control, under the mechanism of reaction control dissolution, for small particles of Al$_2$O$_3$ surrounded by excess liquid, it means that the composition of the surrounding liquid will remain constant, the dissolution rate is therefore proportional to a constant driving force, i.e., the difference between the saturation concentration and the constant liquid concentration, the dissolution rate is therefore proportional to the constant driving force, i.e., the difference between the saturation concentration and the constant liquid concentration, it is found that there is a linear relationship between dissolution time and particle radius, which has nothing to do with particle size and other factors, so dissolution controlled by reaction is not considered. The critical diameter of Al$_2$O$_3$ particles is 560 μm, the dissolution of the Al$_2$O$_3$ particles less than 560μm is controlled by the mass transfer mechanism, and the dissolution of the Al$_2$O$_3$ particles greater than 560μm is controlled by the heat transfer mechanism [21], the in-situ formation of mullite in matrix environment can be compared to mullite in aluminum silicate biphasic gel [22]. The activation energy of mullite formation is 1070kJ/mol by studying the phase transition of mullite in aluminum-silicon two-phase gel mullite, the activation energy of a temperature-dependent nucleation-induced phase prior to nucleation was 987 kJ/mol, and when the particle size of Al$_2$O$_3$ is more than 30 μm, it cannot react completely with SiO$_2$ [23,24].

Based on the above research results, it can be seen that in the development of aluminosilicate castable, mullite is formed in situ by Al$_2$O$_3$ and SiO$_2$ in fine powder to improve the high temperature service performance and thermal shock resistance of refractories, the rate control process of in-situ formation of mullite is the dissolution of Al$_2$O$_3$ particles controlled by mass transfer into SiO$_2$-rich matrix, but the effect of particle size on the in-situ formation of mullite in aluminosiliceous castable has not been further studied, the study of the effect of particle size on the in-situ formation of mullite plays an important role in improving the properties of the material, therefore, on the basis of the above research results, the effect of Al$_2$O$_3$ particle size on the dissolution rate of aluminum silicate castable matrix environment will be established and calculated in this paper, the purpose of this paper is to improve the performance of aluminum siliceous castable by studying the effect of Al$_2$O$_3$ particle size on the in-situ formation of mullite.

2. Calculation model and conditions

The particle size of fine powder in aluminosilicate castable is less than 88 μm, so in this model, it can be equivalent to the dissolution process of Al$_2$O$_3$ powder into SiO$_2$ rich liquid phase under the control.
of mass transfer mechanism, the mass dissolution rate and nuclear shrinkage model \[25\] controlled by mass transfer are used to explain the dissolution mechanism of Al\(_2\)O\(_3\) particles in this paper, and in this model, the change of dissolution rate is calculated by independent particle size of Al\(_2\)O\(_3\). The dissolution process is shown in the figure 1.

\[3\]

**Figure 1.** The dissolution process of independent Al\(_2\)O\(_3\) particle.

Assuming that Al\(_2\)O\(_3\) particles are ideal uniform spherical particles, then the Al\(_2\)O\(_3\) particles satisfy the dimensionless equation (1) in the mass transfer process,

\[Sh = 1 + Re^\frac{1}{2} Sc^\frac{1}{3}\]  

In the equation, \(Sh\) is Sherwood number, \(Sh = kds/D\); \(Sc\) is Schmidt number, \(Sc = V_L/D\); \(Re\) is Reynolds number of Al\(_2\)O\(_3\) particles, \(Re = ud_s/V_L\); \(D\) is the diffusion coefficient of Al\(_2\)O\(_3\) particles in SiO\(_2\)-rich liquid phase, m\(^2\)/s; \(k\) is mass transfer coefficient, m/s; \(d_s\) is the diameter of Al\(_2\)O\(_3\) particles, m; \(V_L\) is the kinematic viscosity of SiO\(_2\)-rich liquid phase, m\(^2\)/s; \(u\) is the relative velocity of Al\(_2\)O\(_3\) particles and SiO\(_2\)-rich liquid phase, m/s.

From this, the equation (2) mass transfer coefficient \(k\) can be obtained,

\[k = \frac{D [1 + 0.3 (\frac{ud_s}{V_L})^\frac{1}{2} (\frac{V_L}{D})^\frac{1}{2}]}{d_s}\]  

The mass transfer control model shows that the driving force for the dissolution of Al\(_2\)O\(_3\) particles is the difference of Al\(_2\)O\(_3\) concentration, that is, the difference between the surface concentration of Al\(_2\)O\(_3\) particles (saturated concentration) and the concentration of Al\(_2\)O\(_3\) in SiO\(_2\)-rich molten solution. Then the expression of the mass change rate of a single Al\(_2\)O\(_3\) particle is given in equation (3) \[26\]:

\[\frac{dm_s}{dt} = k \rho_L (C_s - C_0) \pi d_s^2\]

\(C_s\) and \(C_0\) are saturated mass concentration and initial mass concentration of Al\(_2\)O\(_3\) in SiO\(_2\)-rich electrolyte, %; \(\rho_L\) is the density of Al\(_2\)O\(_3\) particles, kg/m\(^3\);

The equation (4) of the nuclear shrinkage model of independent Al\(_2\)O\(_3\) particle under the same mass transfer condition is as follows,
\[ \frac{d(d_s)}{dt} = -\frac{2k\rho_L(C_s - C_0)}{\rho_s} \]  

\( \rho_s \) is the density of SiO₂-rich molten, kg/m³.

Al₂O₃ was dissolved into the liquid phase rich in SiO₂ with impurities in the aluminosilicate castable matrix, however, the impurities in the matrix of aluminosilicate castable are generally composed of Fe₂O₃, TiO₂, K₂O, CaO, NaO₂ and so on, but the content is small and the Al₂O₃ particles will be agglomerated, therefore, in this model, only the dissolution of independent Al₂O₃ particles in ideal state is considered.

First, the thermodynamic conditions for the in-situ formation of mullite by Al₂O₃ and SiO₂ in the matrix are as follows. According to the Gibbs-Helmholtz formula of thermodynamics, obtain the relationship between \( \Delta rG^\theta \) and temperature:

\[ \Delta rG^\theta = 26.18 - 0.03412T. \]

According to the second theorem of thermodynamics, when \( T > 767K \), Al₂O₃ and SiO₂ can theoretically form mullite, but this is limited to the fact that both Al₂O₃ and SiO₂ are single molecular state and in full contact with each other. In fact, when the temperature is 767K, both Al₂O₃ and SiO₂ are solid particles, It is impossible to make the contact between Al₂O₃ and SiO₂ reach the molecular level, so the actual reaction temperature is much greater than 767K, and the temperature for the formation of non-stoichiometric mullite is 727°C, the formation of mullite can only be observed above 1258°C [27]. The service temperature of Al₂O₃-SiO₂ amorphous refractories is generally above 1400°C, above 1650°C, the nucleation and growth of mullite occurs on the interface between Al₂O₃ and SiO₂, and the growth rate is controlled by the inter-diffusion process of Al³⁺ and Si⁴⁺ through mullite layer [18]. The inter-diffusion coefficient is shown in Table 1.

| Table 1. Diffusion data of Al₂O₃-SiO₂ Melt over 1650°C. |
|-----------------|-----------------|-----------------|-----------------|
|                 | <1870°C         | >1870°C         |                 |
| Cₐl₂o₃ (mol%)   | D₀ (cm²/s)      | Q (kJ/mol)      | D₀ (cm²/s)      | Q (kJ/mol)      |
| 2.53            | 8.03×10⁻²²      | 1268            | 7.00×10⁻¹²      | 857             |
| 5.10            | 1.55×10⁻¹⁸      | 1070            | 1.33×10⁻¹²      | 821             |
| 7.66            | 5.86×10⁻¹³      | 884             | 2.51×10⁻¹¹      | 785             |
| 10.25           | 2.07×10⁻¹¹      | 773             | 2.07×10⁻¹¹      | 773             |
| 15.51           | 5.87×10⁻⁹       | 698             | 5.87×10⁻⁹       | 698             |

Therefore, only the dissolution process in the range of 1400°C ~1650°C is considered in the calculation of this model. F. Verhaeghe [28] combined with the observation of in situ dissolution and lattice Boltzmann dissolution model, the dissolution behavior of Al₂O₃ in CaO-Al₂O₃-SiO₂ liquid is analyzed and compared to the erosion phenomenon of refractories in metallurgical process, and a series of binary diffusion data are obtained, the diffusion coefficient of Al₂O₃ is 4×10⁻¹¹ m²/s at 1450°C.

Dissolution of Al₂O₃ particles into SiO₂-rich solution, the Reynolds number is much less than 1 and almost no flow separation. So it's calculated according to the stokes flow. Under the limit condition of stokes flow Re=0, the mass transfer coefficient k can be approximately \( \frac{d}{ds} \), D is diffusion coefficient and ds is particle radius. Then It can be seen from Equation(3)that the independent alumina particle mass change rate expression is shown in equation (5).

\[ \frac{dm_s}{dt} = D\rho_L(C_s - C_0)\pi d_s^2 \]

\[ = D\rho_L(C_s - C_0)\pi d_s \]  

\[ \text{(5)} \]

The equation (6) of Al₂O₃ nuclear shrinkage model under the condition of equation (4) mass transfer is as follows,
The dissolution process of Al₂O₃ particles into silica-rich molten liquid under the control of mass transfer mechanism needs to be simplified: (1) Al₂O₃ particles are independent and uniform spherical particles. (2) The density of silica-rich melt is 2.2×10³ kg/m³. (3) The diffusion coefficient of Al₂O₃ at 1450°C is 4×10⁻¹¹ m²/s. (4) The true density of Al₂O₃ particles is 3.97×10³ kg/m³.

According to the above model and calculation conditions, the mass change rate of independent Al₂O₃ particles can be calculated as equation (7),

$$\frac{dm}{dt} = 1.985 \times 10^{-7} ds$$

(7)

The expression of Al₂O₃ core shrinkage model is as equation (8),

$$\frac{d (d_s)}{dt} = -\frac{3.184 \times 10^{-11}}{ds}$$

(8)

However, Al₂O₃ in amorphous refractory matrix is not dissolved by a single particle, so it is necessary to analyze and compare the time required for the complete dissolution of Al₂O₃ particles with different particle sizes at the same mass ratio, the equation (9) between the particle size of different Al₂O₃ and the time required for complete dissolution in the matrix environment is derived by using equation (8),

$$\int \frac{d(d_s)}{dt} = -\int \frac{3.184 \times 10^{-11}}{ds}$$

(9)

### Table 2. Mass dissolution rate, nuclear shrinkage rate and complete dissolution time corresponding to typical particle size.

| ds (μm) | dm/dt (g/s) | d(ds)/dt (μm/s) | t (s) |
|---------|-------------|-----------------|-------|
| 1       | 1.985×10⁻¹⁰ | 31.84           | 0.016 |
| 10      | 19.85×10⁻¹⁰ | 3.184           | 1.57  |
| 20      | 39.70×10⁻¹⁰ | 1.592           | 6.27  |
| 30      | 59.55×10⁻¹⁰ | 1.061           | 14.11 |
| 40      | 79.40×10⁻¹⁰ | 0.796           | 25.08 |
| 50      | 99.25×10⁻¹⁰ | 0.637           | 39.19 |
| 60      | 119.10×10⁻¹⁰| 0.531           | 56.43 |
| 70      | 138.95×10⁻¹⁰| 0.455           | 76.80 |
| 80      | 158.80×10⁻¹⁰| 0.398           | 100.31|

3. Results and analysis

The particle sizes of Al₂O₃ particles are 1μm, 10μm, 20μm, 30μm, 40μm, 50μm, 60μm, 70μm, 80μm, respectively, and the calculation results are shown in Table 2.

The data shown in Table 2 show the mass dissolution rate, nuclear shrinkage rate and complete dissolution time of Al₂O₃ particles in fine powder at 1450°C. The service temperature of aluminum siliceous castable is generally below 1650°C, and the temperature dependence of diffusion coefficient is often described by Arrhenius formula.
From the Arrhenius formula, it can be seen that the diffusion coefficient increases with the increase of temperature. From equation (5) (6), it can be seen that when the particle size is constant, the change rate of particle mass and the rate of nuclear shrinkage increase with the increase of diffusion coefficient, and can also be expressed as increasing with the increase of temperature. The results are the same as the results obtained by studying the dissolution behavior of Al₂O₃ in continuous casting slag by rotating cylinder method [29] and analyzing the dissolution behavior of Al₂O₃ in CaO-Al₂O₃-SiO₂ slag by quantitative phase field model [30]. The results show that the formation rate of in-situ mullite increases with the increase of the service temperature of aluminosilicate castable.

![Figure 2](image_url)

**Figure 2.** (a) Variation curve of mass dissolution rate of independent Al₂O₃ particles with Al₂O₃ particle size (b) Variation curve of nuclear shrinkage rate versus Al₂O₃ particle size.
The variation of the mass change rate of the individual Al$_2$O$_3$ particles with the particle size of the Al$_2$O$_3$ may be shown in figure 2 (a), with the increase of the particle size of Al$_2$O$_3$ in fine powder, the mass dissolution rate of single particles increases because of the increase of dissolution surface area in the matrix; the variation of the core shrinkage rate of the Al$_2$O$_3$ particles with the particle size of the Al$_2$O$_3$ can be schematically shown in figure 2 (b), with the increase of the particle size of Al$_2$O$_3$ in fine powder, the nuclear shrinkage rate of Al$_2$O$_3$ particles slows down, and the decrease of nuclear shrinkage rate is the most obvious when the particle size increases from 1 $\mu$m to 10 $\mu$m.

![Figure 3. Variation of complete dissolution time of independent Al$_2$O$_3$ with Al$_2$O$_3$ particle size.](image)

The dissolution of the whole Al$_2$O$_3$ particles in the matrix determines the formation rate of in situ mullite, while the dissolution of the same mass and well dispersed Al$_2$O$_3$ particles is determined by the dissolution time of a single Al$_2$O$_3$ particle. It can be seen from figure 3 that the complete dissolution time of the independent Al$_2$O$_3$ micro powder particles in the matrix environment of the aluminum-silica castable increases with the increase of the size of the Al$_2$O$_3$, and the rate of complete dissolution increases with the increase of the particle size; when the Al$_2$O$_3$ particle size was 80 $\mu$m, the total dissolution of the individual particles required 100.31 seconds, the total dissolution time required when the particle size was 8$\mu$m was only 1.00 seconds, and when the particle size reached 1$\mu$m, the individual particle dissolves almost instantly.

4. Conclusions
The in-situ formation of mullite in aluminosiliceous castable matrix has a great influence on the high temperature performance of refractories, while the particle size of Al$_2$O$_3$ in fine powder has a decisive effect on the rate of in-situ formation of mullite. The mass dissolution rate and the nuclear shrinkage rate of the Al$_2$O$_3$ particles are increased with the use of the temperature; The formation rate of mullite in situ decreased rapidly when the particle size of Al$_2$O$_3$ was 10 $\mu$m, and changed little when the particle size was more than 10$\mu$m; The shorter the grain size of the Al$_2$O$_3$ micro-powder in the whole aluminosiliceous castable, the shorter its complete dissolution time indicates that the in-situ rate of mullite in the whole matrix increases with the decrease of the grain size of Al$_2$O$_3$, when the particle size is below 8$\mu$m, the formation of in-situ mullite can be completed in 1.00 seconds. The dissolution law of the above Al$_2$O$_3$ powder can be widely used in the process of controlling the in situ formation rate of mullite in amorphous refractory matrix by dissolution mechanism, therefore, the particle size
distribution of Al$_2$O$_3$ powder in aluminosiliceous castable can be better studied and adjusted in the following work, so as to improve the performance of castable.

References

[1] Zhou N S, Hu S H and Zhang S H 2004 *Refractories* **38** 196
[2] Nouri-Khezrabad M, Braulio M A L and Pandolfelli V C 2013 *Ceram Int.* **39** 3479
[3] Studart A R, V C Pandolfelli, Tervoort E and Gauckler L J 2010 *J Am Ceram Soc.* **85** 1947
[4] Zhang W 2009 *Shandong Ceramics* **32** 34
[5] Zhang X, Shen S H, Liu J C and Xie Y H 2005 *Refractories* **39** 354
[6] Zawrah M F M, Khalil N M 2001 *Ceram Int* **27** 689
[7] Ruan G, Zhang Z and Yin M 2011 *Rare Metal.* **30** 506
[8] Li H B, Zhao J Z and Chen Q 2007 *Refractories.* **41** 435
[9] Li H B, Zhao J Z and Chen Q 2008 *Refractories* **42** 40
[10] Li L S, Ping Z F 2006 *Bulletin of The Chinese Ceramic Society* **25** 34
[11] Shi G, Zhang W and Xiong X Y 2010 *Refractories* **44** 325
[12] Wang Y Y, Yan W, Li N, Zhang Z Y and Hu Y D 2017 *Refractories* **51** 246
[13] Wang Y Y, Yan W and Li N 2017 *China’s Refractories* **26** (2) 39
[14] Li P J, Li L, He Z Y, Peng X Y and Yang F R 2011 *Refractories* **45** 166
[15] Feng S S, Zhou N S 2011 *China’s Refractories* **20** 18
[16] Li Z G, Zhang Z Y, Lu Z C and Song W P 2011 *China’s Refractories* **20** (1) 1
[17] Zhao S K, Huang Y, Huang X X and Guo J K 2002 *J Ceram.* **23** (3) 149
[18] Saruhan B, Albers W, Schneider H and Kaysser W A 1996 *J Eur Ceram Soc* **16** 1075
[19] Sankaran S, Ilhan A A 1991 *J Am Ceram Soc.* **74** 2388
[20] Yu J, Yang Q M, Yang Z F and Chen Y R 1998 *Journal of the Chinese Ceramic Society* **26** 578
[21] Li M, Bai X, Li Y, Hou W Y and Bai Y T 2016 *The Chinese Journal of Nonferrous Metals.* **26** 455
[22] Zhao H L, K Hiragushi and Y Mizota 2003 *J Sol-Gel Sci Technol.* **27** 287
[23] Wei W C, Halloran J W 1988 *J Am Ceram Soc.* **71** 581
[24] Wei W C, Halloran J W 1998 *J Am Ceram Soc.* **71** 166
[25] Hou W Y, Li M, Li Y and Bai X 2015 *Light Metals.* (4) 24
[26] Thonstad J 1988 *Light Metals.* 105
[27] Zhou B 2014 *The study of monophasic mullitization’s reaction mechanism (Wuhan University Of Technology)*
[28] Verhaeghe F, Liu J , Guo M 2007 *Appl Phys Lett.* **91** 620
[29] Bui A H, Ha H M, Kang Y B, Chung I S and Lee H G 2005 *Met Mater Int.* **11** 183
[30] Liu J J, Zou J, Guo M X and N Moelans 2016 *Comput Mater Sci.* **119** 9