Effect of AlF₃ Content on the Properties of In-situ Generated Mullite Whisker Reinforced High Aluminum Castables

Jijia Li, Xudong Luo*, Zhipeng Xie, Mengmeng Yang

*School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan 114051, China

Corresponding author: luoxudongs@aliyun.com

Abstract. The mullite whiskers have excellent high temperature resistance and high heat characteristics, the melting point is above 2000°C, and the maximum use temperature is 1500°C to 1700°C. In this paper, mullite whiskers were prepared by in-situ growth method. High aluminum castables were prepared by injecting mullite whiskers in situ at high temperature by adding Al(NO₃)₃·9H₂O and NH₄F to high alumina castables. It is 0, 0.5 wt%, 1 wt%, 2 wt%, 4 wt%. The materials were mixed, stirred, cast, and demolded and then fired at 1400°C. By testing the bulk density, apparent porosity and residual flexural strength of the samples, the properties, microstructure and microstructure of the fired samples were analyzed and characterized by means of XRD and SEM. The study focused on AlF₃ to mullite whiskers. The effect of microstructure and flexural strength. The results show that the introduction of AlF₃ promotes the formation of mullite whiskers. With the increase of AlF₃ content, the aspect ratio of whiskers increases first and then decreases, and when the AlF₃ content is 1wt%, the aspect ratio of whiskers The maximum is 6.67. Excessive AlF₃ causes the mullite whiskers to become thick and rod-shaped. The in-situ mullite whiskers form an interlocking structure, which enhances the flexural strength of mullite high-aluminum castables when AlF₃ content When the weight is 1wt%, the flexural strength of the model reaches the maximum value of 35.92MPa, and the residual flexural strength of the sample after 5, 10, and 15 thermal shocks reaches the maximum, which are respectively 2.07 MPa, 1.95 MPa, 1.19 MPa.

1. Introduction

The growing application of and demand for refractory castables as an alternative to conventional bricks have encouraged researchers and manufactures to investigate the materials in depth and to improve it continuously. Physical, chemical and mechanical properties of refractory castables at different temperatures as well as their processing and bonding mechanism are the focus of such investigations.

Substantial increase in the service life of alumina based castables has been observed over the past few decades, mainly because of the gradual decrease of their cement content. Refractory cement is conventionally and commonly used as a binder for castables but is not applicable for high temperature applications due to the formation of low melting eutectics. So the focus has now been shifted to cement free bonding systems for high temperature applications.[1–6] Colloidal silica as a binder (using sol–gel based coagulation bonding) has been reported by many authors. Sol-gel bonding system...
is more advantageous than other systems due to easier processing no requirement of any property modifying additive. The presence of ultrafine silica particles in alumina castable system form mullite bonds at high temperatures and improve the properties of the castables. But the chances of presence of free silica and formation of liquid phase above the eutectic temperature in Al₂O₃-SiO₂ system have restricted and limited its use for very high temperature applications [7–12]. So, some methods for reinforcing castables have emerged. This experiment uses a method of in situ formation of mullite whiskers to enhance high alumina castables. This method can effectively solve the agglomeration of external whiskers.

This experiment used mullite whiskers. In order to prepare high-performance mullite, the conventional method is to mix Al₂O₃ and SiO₂, and then melt in an electric furnace at 2000°C or higher, and pour the melt into a mold to cool to room temperature to obtain "melted mullite". Or Al₂O₃ and SiO₂ raw materials were powdered and thoroughly mixed, and then sintered in a furnace at 1700°C to obtain "sintered mullite". In recent years, in order to meet the needs of industry, people pay more and more attention to the chemical synthesis of pure phase mullite at low temperature, that is, the aluminum and silicon raw materials are uniformly mixed to form a composite powder, which is used as a mullite precursor and then sintered. Made of mullite, the mullite obtained by this method is called "chemical mullite". Okada et al.[13] calcined Al₂O₃-SiO₂ xerogel prepared from tetraethyl orthosilicate and aluminum nitrate in a closed container to synthesize mullite whiskers. When the temperature is raised from 1100°C to 1600 °C, whiskers along the C-axis direction, whisker length increased from 7μm to 10μm, and the aspect ratio decreased from 25 to 10. Yuan Jianjun et al.[14] prepared chemically pure ethyl silicate, water, aluminum nitrate and aluminum fluoride as raw materials, ethanol as solvent, hydrochloric acid and ammonia as catalyst for preparing gel to prepare mullite whiskers, Al(NO₃)₃:A1F₃:TEOS=9:3:4 (by mole), wherein fluorine in the aluminum fluoride functions as a growth catalyst for mullite whiskers. Perera [15] and Katsuk [16] calcined kaolinite (2SiO₂·Al₂O₃·2H₂O) above 1600 °C (the lowest eutectic point of silica and mullite is 1587°C), and mullite was synthesized from the melt. Katsuki et al.[17] decomposed ceramic clay ore at 1400-1600°C to obtain mullite whiskers on the surface of alumina particles, with a length of 50-200μm and a diameter of 1-3μm. A large number of studies have shown that toughening and strengthening the material by whiskers is one of the effective ways. At present, the focus of research is mainly to introduce whiskers from the outside into the matrix material. Although the toughening and reinforcing effect is remarkable, there are a series of shortcomings such as difficulty in dispersing whiskers, poor uniformity of distribution, difficulty in sintering, and harmful to human health. Therefore, in recent years, new materials self-reinforcing technology has attracted people's attention. For example, some basic techniques are used to form in-situ growth whiskers and other irregular crystal phases in the high-temperature treatment process to achieve the purpose of toughening and reinforcing. Cai Shu et al.[18] prepared the mullite precursor by hydrolysis-precipitation method using ethyl orthosilicate and crystalline A1C1₃·6H₂O as raw materials, and then added AlF₃ to the mullite precursor and heat-treated under closed conditions to form Mo. Come to the stone whiskers. Mu Baichun et al. used alumina, zircon and aluminum fluoride as the main raw materials to prepare austerite whiskers by in-situ reaction synthesis. The whiskers are round needle-shaped and have a diameter of 0.2-1.0 μm. The diameter ratio is 8 to 30. But the distribution of whiskers is not very uniform. So this experiment designed a new way to add a uniform effect to the distribution of whiskers, while finding the best amount of addition.

2. Experimental

2.1. Materials and processing
The average grain size of the high alumina castable matrix was 600nm, It comes from Henan Jiuyuan Environmental Protection Technology Co., Ltd. Al(NO₃)₃·9H₂O and NH₄F are selected from Sinopharm Chemical Reagent Co., Ltd. High alumina castables are chemically analyzed that it
contains significant quantities of Al₂O₃ (63.74%) and SiO₂ (29.48%) as well as other oxides such as CaO (0.67%), MgO (1.11%), Fe₂O₃ (1.60%), NaOH (1.90%) and TiO₂ (1.50%).

According to the chemical equation: \( Al(NO₃)₃ + NH₄F \rightarrow AlF₃ + NH₃ \cdot H₂O \), and calculate the amount of Al(NO₃)₃ and NH₄F according to the mass fraction of AlF₃. The prepared solutions were added to the matrix of high-alumina castable, and add enough water to mix well. For pouring molding, use a 10 × 10 × 50 strip mold. The cast mold will be placed in room temperature drying 24 hours after the mold, and then placed in 110°C electric blast drying box drying for 24 hours. Put it into the electric heating box furnace and keep it at 1400°C for 3 hours. Then take out the sample.

2.2. Characterization

Densification parameters in terms of bulk density and apparent porosity of the obtained AT composites were determined by Drainage method of Archimedes. In order to understand the effect of the catalyst before and after the addition of the catalyst on the porosity of the sample. Compressive strength (CCS) of the sintered specimens was carried out by placing each specimen into two load blocks. The alignment of the specimens in the load blocks was ensured.

Anti-folding test on sintered samples. The experiment is to use the standard after burning (10 mm × 10 mm × 50 mm). The phase composition of sintered samples with different structures were characterized by XRD(Philips X-pert-MPD, Holland). And the microstructure was examined on a field emission scanning electron microscope (Zeiss SIGMAHD, Germany). The water quench test was performed by recording the number of quenching to evaluate the thermal shock resistance, and the process was repeated until the sample was broken (the sample was heated to 1100°C for 30 min, and then rapidly immersed in water).

![Figure 1. XRD patterns of 4% high alumina samples treated with additives at different temperatures.](image)

3. Results and discussion

3.1. Effect of AlF₃ content on phase composition of high alumina castables

Figure 1 shows the XRD pattern of a high aluminum castable with 4wt% AlF₃ added at different temperatures. Sample No.1 stands for 1100°C, sample No.2 stands for 850°C, sample No.3 stands for 645°C, and sample No.4 stands for 357°C. As can be seen from Fig 3.3, the mullite phase (Al₆Si₂O₁₃),
quartz phase (SiO$_2$), and corundum phase (Al$_2$O$_3$) were detected after sintering at different temperatures. And the diffraction intensity of quartz phase increases with the increase of temperature, the intensity of diffraction peak of mullite increases first and then decreases, and the intensity of diffraction peak of corundum increases first and then decreases.

3.2. Effect of AlF$_3$ content on microstructure of high alumina castable matrix

Figure 2 shows the effect of AlF$_3$ on the microstructure of the sample. It can be observed from the figure that the microstructure of the sample changes significantly with the addition of AlF$_3$. Figure 2 (a) is a sample without AlF$_3$, basically no mullite whiskers are observed. When the addition amount of AlF$_3$ is 0.5wt%, a small amount of mullite whiskers can be observed faintly. When the addition amount of AlF$_3$ is 1wt%, the microstructure of the sample changed significantly, a large number of acicular fine mullite whiskers were observed in the sample, and the whiskers were intertwined into a network structure, and the aspect ratio of the whiskers was 6.67. When the amount of AlF$_3$ added is increased to 2wt%, the mullite whiskers are obviously observed to be thick and rod-like. When the amount of AlF$_3$ is 4wt%, a large amount of columnar mullite can be observed, and the diameter of the crystal grains is observed. It also increases with a diameter of 2-2.2μm.

![Figure 2](image_url)
According to the analysis, when the sample is fired at 1400 °C, the in-situ synthesized solid phase AlF₃ sublimation reacts with Al₂O₃ and SiO₂ in the raw material to promote the raw material mullite, and mullite grows to form whiskers. The equation is as shown in (1) to (4). When the content of AlF₃ is small, the vapor phase AlF₃ formed by sublimation is insufficient, that is, the fluoride formed by the reaction is insufficient, and the directional growth of whiskers is restricted. When the content of AlF₃ is too much, the amount of gas phase generated is too large, and excessive fluoride will cause the mullite whiskers to become coarse, so that the aspect ratio of whiskers is reduced.

\[
\begin{align*}
6\text{AlF}_3 + 3\text{O}_2 & \rightarrow 6\text{AlOF} + 12\text{F} \\
\text{Al}_2\text{O}_3 + 2\text{F} & \rightarrow 2\text{AlOF} + 0.5\text{O}_2 \\
2\text{SiO}_2 + 8\text{F} & \rightarrow 2\text{SiF}_4 + 2\text{O}_2 \\
6\text{AlOF} + 2\text{SiF}_4 + 3.5\text{O}_2 & \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 14\text{F}
\end{align*}
\] (1) to (4)

![Figure 3. Porosity and bulk density map of high alumina castables.](image)

### 3.3. Effect of AlF₃ content on sintering properties of high alumina castable matrix
#### 3.3.1 Appreciable porosity and bulk density

Figure 3 shows the effect of different AlF₃ additions on the apparent porosity and bulk density of high alumina castables. It can be seen from the figure that the apparent porosity of high alumina castables increases with the increase of AlF₃ addition, and the change of bulk density is opposite, and the apparent porosity reaches the maximum when AlF₃ is added at 4wt%. The value was 43.06% and the bulk density reached a minimum of 1.67 g/cm³.

According to the following chemical reaction equation analysis, it is considered that a series of chemical reactions between Al(NO₃)₃ and NH₄F produce NH₃ and HF gas during the process of generating AlF₃. As the amount of AlF₃ is increased, the amount of gas generated increases. The apparent porosity of the high alumina castables gradually increases and the bulk density gradually decreases. In addition, it can be seen from the analysis of 3.2 that during the calcination of the sample, AlF₃ reacts with the raw material to form a vapor phase fluoride. When the content of AlF₃ is too large, the amount of gas phase generated is excessive, and the remaining fluoride is discharged as a gas. Therefore, the excessive addition of AlF₃ adversely affects the apparent porosity and bulk density of the high alumina castable.

\[
\text{Al(NO}_3\text{)}_3(s) + \text{NH}_4\text{F}(s) = (\text{NH}_4)_2\text{AlF}_6(s) + 3\text{NH}_3\text{NO}_3
\] (5)
\[(NH_4)_3AlF_6(s) = NH_4AlF_4(s) + 2NH_3(v) + 2HF(v) \quad (6)\]

\[NH_4AlF_4(s) = AlF_3(s) + NH_3(v) + HF(v) \quad (7)\]

**Figure 4.** Residual bending strength map of high alumina castable.

### 3.3.2 Residual bending strength after thermal shock

Figure 4 shows the effect of different AlF₃ additions on the residual flexural strength of high alumina castables after thermal shock. It can be seen from the figure that the flexural strength of the high-aluminum castables increases first and then decreases with the increase of the addition amount of AlF₃. When the addition amount of AlF₃ is 1wt%, the flexural strength is the highest, reaching 35.92MPa, and the heat is high. The residual flexural strength of high alumina castables with 1wt% AlF₃ addition after 5, 10, and 15 shocks was the highest, 2.07MPa, 1.95MPa, and 1.19MPa, respectively. It can be seen that the residual flexural strength of the high alumina castable is best when the addition amount of AlF₃ is 1wt%.

According to the SEM spectrum and the analysis of the apparent porosity and volume density curves, it is considered that when the amount of AlF₃ added is small, the flexural strength of the sample is low. Although the porosity of the sample is relatively low, no whisker is generated at this time. It can be seen that whiskers play a dominant role in the flexural strength of the sample; when the amount of AlF₃ is too large, the amount of whiskers increases as the amount of AlF₃ increases, and the whiskers become coarse, which makes the sample the flexural strength is reduced. In addition, the reduction of the flexural strength is also related to the excessive porosity of the sample; only when the amount of AlF₃ added is moderate, the fine interdigitated mullite whiskers are produced in the sample, which is beneficial to The sample is resistant to folding and has a good porosity and exhibits good bending resistance.

### 4. Results and discussion

1. Al(NO₃)₃ reacts with NH₄F at high temperature to form AlF₃ and produces gas. As the content of AlF₃ increases, the apparent porosity of the aluminum castable increases gradually, and the bulk density decreases gradually. When the AlF₃ content is 4wt%, the apparent porosity reached a maximum of 43.06%, and the bulk density reached a minimum of 1.67 g/cm³.

2. The addition of AlF₃ is beneficial to the formation of mullite whiskers. With the increase of AlF₃ content, the amount of mullite whiskers is increased, but the aspect ratio of mullite whiskers is gradually decreasing. When the AlF₃ content is 1% by weight, the aspect ratio reaches a maximum value of 6.67.
(3). The flexural strength of high alumina castables increases first and then decreases with the increase of AlF₃ content. When the AlF₃ content is 1wt%, the flexural strength reaches a maximum of 35.92MPa; the residual flexural strength after thermal shock. The same trend is also observed. The flexural strength of the high aluminum castable with 1wt% AlF₃ content after 5, 10, and 15 thermal shocks is the maximum.

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