# Strengthening and Toughening of Mullite-Silicon Carbide Refractory with AlN whiskers Used in CDQ

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## ABSTRACT

The strengthening and toughening effect of AlN whiskers in-situ generated in mullite-SiC refractories were studied and examined. The results show AlN whiskers are in-situ formed and interact to networks in the matrix when metal aluminum powder was added into the mullite-SiC refractories after heat treatment under temperature more than 850℃ for 8h in nitrogen flowing. The strengths of CMOR and CCS increase evidently as firing temperature increase, and reach the maximum values at 1000°C. The bending strength at 1000°C increase more than three times, the residue strength ratio of CMOR after thermal shock increases from 59% to 74%, the toughness also greatly improved by AlN whiskers.

## KEY WORDS

Coke dry quenching, In-situ formation, AlN whisker, strengthening and toughening,

## 1 INTRODUCTION

The technologies of coke dry quenching (CDQ) about energy saving and environmental protection have been promoted strongly. Nitrogen is blown into coke dry quenching furnace as the cooling gas. Inclined pillar which endures the high erosive wear， thermal shock and weight of refractories above it at the same time， is the key part of CDQ[1]. Along with the development of CDQ technology, the refractories for CDQ inclined pillars have developed from dense fireclay brick to mullite brick an then to mullite-silion carbide brick[2]. Mullite-silicon carbide brick is the main refractory and widely used in practical CDQ[3]. The average surviving life of mullite-silicon carbide brick is about 2 years because of low strength and toughness. Although some refractories, such as $Si_3N_4$ bonded SiC brick, were fabricated as substitute. No one of them has been widely used in CDQ because of the complicated preparation process, high cost or low toughness[4,5].

Introduction of whiskers or fibers into refractory is an effective method for strengthening and toughing and has been widely used by researchers[6]. However, the preparation of whiskers or fibers is a complex and high cost process. Whiskers and fibers are harmful to body either in preparing or using because they are too small to be protected from being inhale[7]. So, in-situ synthesis of whiskers during material preparing or being used is an ideal method.

Considering the advantages and problems discussed above, this paper fabricated a kind of mullite-silicon carbide refractory reforced by AlN whiskers which was in-situ synthesized during serving in CDQ. The Phase composition, microstructure and physical properties were also analyzed.

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## 2 EXPERIMENTS

### 2.1 Materials and preparation of samples

In this paper, sintered mullite (particle size: 5-3mm, 3-1mm, 1-0mm, 0.074mm) and silicon carbide (particle size: 3-1mm, 1-0mm, 0.074mm) were used as refractory aggregates, α-$Al_2O_3$ micro powder (1-5μm) and micro silica were used as matrix materials. All these raw materials were used directly without purification. Phenol resin was used as a binder. Metallic Al powder (38μm) and Silicon powder were added as additives. The detailed compositions are shown in Table 1.

**Tab.1 Compositions of samples**

| Material | Material content in two Samples /wt% | |
|---|---|---|
| | $A_0$ | $A_1$ |
| Sintered mullite | 56 | 50 |
| Silicon carbide | 32 | 32 |
| α-$Al_2O_3$ micro-powder | 7 | 7 |
| Micro-silica | 3 | 3 |
| Phenol resin | 4 | 4 |
| Metallic Al powder | 0 | 6 |

Raw materials were mixed homogenously and then pressed into bar-shaped samples at 100 MPa. The pressed samples were cured at 200 °C for 24 hours and then fired in nitrogen under 600°C, 850°C, 000 °C and 1200°C for 8 hours, respectively. The nitrogen gas purity is above 98 wt%.

### 2. 2 Testing and characterization methods

The phase compositions of the samples were determined through X-ray diffraction (XRD; X′ Pert Pro). The microstructures of ruptured surfaces were observed by field emission scanning electron microscope (FESEM; Nova NanoSem 400) equipped with an energy dispersive Xray spectroscope (EDS; Phoenix). The apparent porosity (AP) and bulk density (BD) of samples were measured according to Archimedes' principle with kerosene as medium. The cold modulus of rupture (CMOR) and flexural modulus were measured using the three-point bending test at ambient temperatures with a span of 80 mm and a loading rate of 0.5 mm/min by means of an electronic digital control system (EDC120; DOLI Company, Germany); the force-displacement curves were recorded simultaneously during the test. The thermal shock resistance of samples was evaluated with the method of water quenching. The samples were heated at 1000 °C for 0.5 hour in reducing atmosphere and then put into the water at room temperature for 5 min. The samples were dried, and their residual cold bending strength was measured after five thermal shock cycles. The residual strength ratio (RSR) was calculated. The hot modulus of rupture (HMOR) of the samples heated at 1000°C was measured in reducing atmosphere using the three-point bending test.

The mechanical behavior was determined according to the stress-deformation curves which were measured in an electrical furnace with $Mo_2Si$ heating elements. The testing samples were shaped in bar and compressive loading was imposed at the middle of sample, the related deformation was detected at the same time. The test stared from room temperature according to a spiral heating process with heating rate of 5℃/min and retain for 10 minutes every 200 ℃. Meanwhile, loading-unloading cycles were implied with the rate of 0.15MPa/s, maximum load was calculated according to the CMOR, the loads and deformations were recorded every 1MPa, until the sample fracture or heating up to 1400℃. This test schematic is illustrated in Fig.1

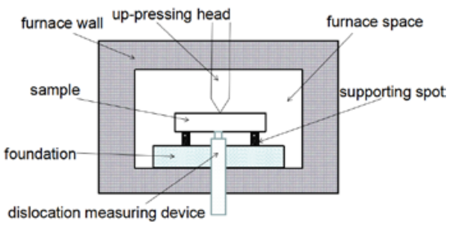



**Fig.1 Schematic of stress-deformation test**

## 3 RESULTS AND DISCUSSION

### 3.1 Phase composition and microstructure analysis

Fig. 2 shows the XRD patterns of mullite-SiC refractory after heat treatment with different temperatures in nitrogen. It is shown that the major phases of specimens are mullite and silicon carbide. The peaks of metallic Al is detected at 600℃. The peak of metallic Al disappears and the peaks of AlN appear when the heating temperature rises to 850℃. AlN peaks become stronger along with the increase of heating temperature. The phenomena indicate that AlN cannot be formed at 600℃ and can in-situ formed higher than 850℃.

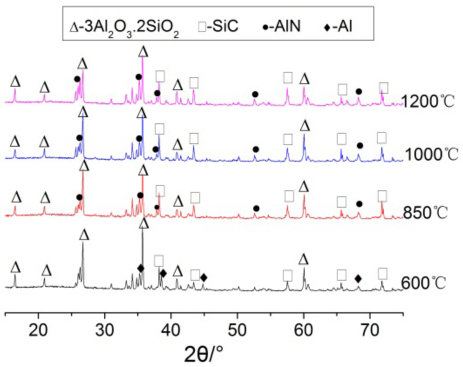



**Fig.2 XRD patterns of samples after nitriding at different temperatures**

Fig.3 shows the SEM micrographs of the ruptured surfaces of samples fired after different temperatures. It can be seen that the metallic Al powder exist as metal phase after 600℃ heat treatment, metallic Al powder has been nitrogenized into hexagonal AlN with 0.2μm~1μm length when heating temperature rises to 850℃. When heating temperature rises further to 1000 ℃ and 1200 ℃, AlN whiskers which lengths are 2μm~10μm, diameters are 5nm~100nm, formed and interact each other forming networks in the matrix.

The ceramic phases AlN are formed acording to Eq. (1)[8]:

$$2Al(l)+N_2(g)=2AlN(s) \quad (1)$$

$$\Delta G^0=-328946+117.05T \text{ (J)}$$

Al powder fuses at 660℃and exists as liquid phase. The Gibbs free energy of Eq. (1) at 660 °C is −226.76 kJ, and $N_2$ could directly react with aluminum liquid to form the AlN phase. With the heating temperature increasing, the reaction rate increases, and AlN grows along the direction of axial and forms to the whisker.

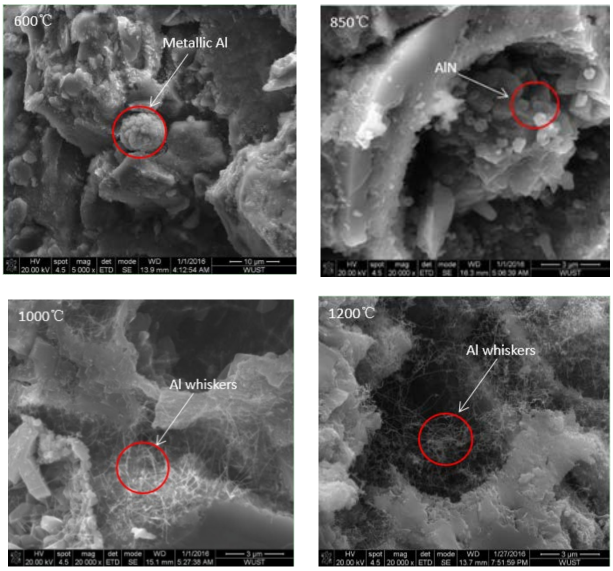



**Fig.3 SEM micrographs of samples nitriding after different temperatures**

### 3.2 Properties of mullite-SiC refractories

The quality change, apparent porosity and bulk density of mullite-SiC refractories fired under different temperatures for 8 hours are shown in Fig.4, Fig.5 and Fig.6 respectively. It can be seen the quality change of sample without Al powder addition decrease because of thermal decomposition and volatilization at high temperatures. While the quality change of sample with Al powder addition increases from -0.65% to +0.36% as temperature increases from 600℃ to 1000℃.

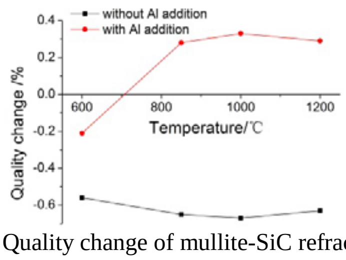



Fig. 4 Quality change of mullite-SiC refractories

As the temperature increases from 600 °C to 1200 °C, the bulk density decreases at first and then increase for sample without Al powder addition, ant an opposite change appears for sample with Al powder addition. This phenomenon indicates that $N_2$ participates in the reaction and AlN are formed which is verified by Fig.2 and Fig. 3.

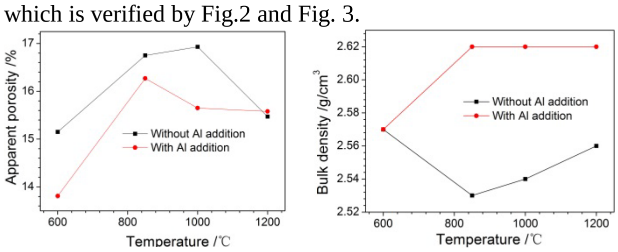



Fig. 5 Apparent porosity and bulk density of mullite-SiC refractories

The CMOR and CCS of mullite-SiC refractories fired under different temperatures are shown in Fig. 6. It can be seen that the CMOR and CCS of samples with aluminum powder addition increase evidently as firing temperature increase, and reach the maximum values at 1000°C. The maximum values of CMOR and CCS are about four times compared with those of samples without aluminum addition. When the firing temperature reaches to 1200°C, the values of CMOR and CCS decrease slightly for samples with aluminum powder addition, but they increase for samples without aluminum powder addition. This can attribute to the AlN whiskers in-situ created in the matrix as seen in Fig.3. AlN whiskers interact and form networks in the matrix, the refractory is strengthened dramatically.

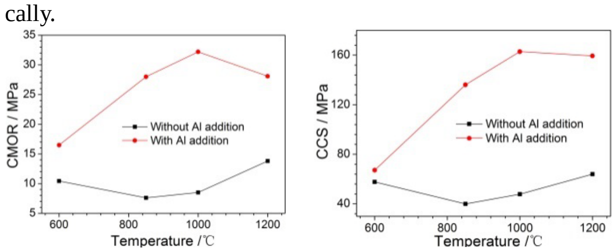



Fig. 6 CMOR and CCS of mullite-SiC refractories

Tab.3 shows the HMOR of the samples heated at 1000°C and the residual strength ratio after thermal shock. It can be seen that the HMOR at 1000°C increase more than three times for samples with aluminum powder addition, and the residue strength ratio increases from 59% to 74%. This demonstrates the thermal shock resistance highly increases.

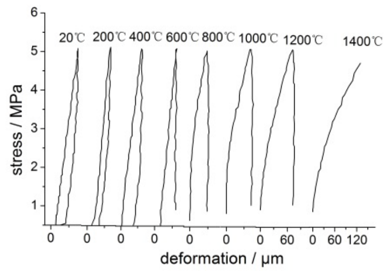
Tab. 3 HMOR at 1000°C and RCMOR after thermal shock of mullite-SiC refractories

| Index | $A_0$ | $A_1$ |
|---|---|---|
| HMOR /MPa | 9.6 | 39.6 |
| RCMOR /% | 59 | 74 |

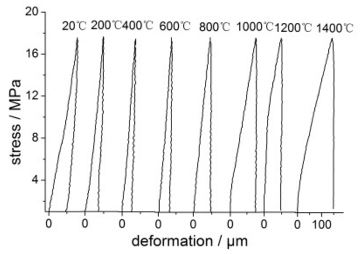
### 3.3 Mechanical behavior of mullite-SiC refractories

The stress-deformation curves are shown in Fig. 4. It can be seen that the mechanical-behavior of mullite-SiC refractory can be divided into three stages: the lower temperature stage of 20℃~800℃, the small deformation is almost reversible in loading–unloading cycle; the stage of 800℃~1200℃, deformation increases as loading increases and the maximum deformation appears at the beginning of unloading and some permanent deformation retained in the specimen after every cycle; the last stage of 1200℃~, the residual permanent deformation continuously increases after loss of loading until the sample breakdown.

However, significant differences in mechanical behavior exist between the samples with aluminum powder addition ($A_1$) and without aluminum powder addition ($A_0$). The maximum stress for $A_1$ is 18MPa while it's only 5MPa for $A_0$. And after 7 loading-unloading cycles, when the temperature is up to 1400℃, the samples without aluminum powder addition are failure, while the sample with aluminum powder addition can still withstand the stress. So, AlN whiskers in-situ formed in the matrix improve the toughness of refractories.




(a)




(b)

**Fig.4 Stress-deformation curves of mullite-SiC refractories, (a) Samples without Al powder addition and (b) Samples with Al powder addition**

## 4. CONCLUSIONS

1) AlN whiskers were in-situ formed and interact each other forming networks in the matrix when metal aluminum powder was added into the mullite-SiC refractories and firing under temperatures of 850℃, 1000℃ and 1200℃ for 8h respectively in nitrogen flowing.

2) The CMOR and CCS of samples with aluminum powder addition increase evidently as firing temperature increase, and reach the maximum values at 1000°C which are about four times compared with those of samples without aluminum addition. The bending strength at 1000°C improves more than three times, the residue strength ratio of CCS increases from 59% to 74%.

(3) The stress-deformation curves show the mechanical-behavior of mullite-SiC refractories can be divided into three stages. AlN whiskers in-situ formed in the matrix improve the toughness of refractories.


## Acknowledgements

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