Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

In situ synthesis of AlN whiskers in mullite-silicon carbide refractory under simulated coke dry quenching conditions

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ARTICLE INFO

Keywords:
AlN whiskers
Coke dry quenching
Refractories
Nanoscale Fe

ABSTRACT

AlN whiskers in mullite-silicon carbide refractories were synthesized under the simulated conditions of service temperature and nitrogen flow in a coke dry quenching (CDQ) furnace. Nanoscale Fe powder and Si_3N_4-Fe powder were added as catalysts to the raw materials of the mullite-silicon carbide refractory containing metallic Al powder. The correlation between the microstructures and the sample properties were studied; the results showed that the formation and interaction of AlN whiskers *in situ* in the matrix improved the strength, thermal shock resistance, and toughness of the refractory. Nanoscale Fe powder was more effective as a catalyst for the formation and growth of AlN whiskers. The formation temperature of AlN whiskers in the samples containing nanoscale Fe powder was successfully decreased from 1000 to 850 °C under nitrogen flow.

1. Introduction

Coke dry quenching (CDQ) systems have been widely used in steel plants because they produce high-strength coke, consume less energy, and are environment friendly. The CDQ furnace is the core component of a CDQ system, and cantilevers made of refractories are the critical components of a CDQ furnace. These cantilevers support the upper weight of the refractories and endure the highly erosive wear caused by red-hot coke and circulating gas. Mullite-silicon carbide brick is often used as the material for cantilevers in CDQ furnaces. However, its average service lifetime is only about two years because of its low strength and poor toughness [1]. Therefore, the advantages of the CDQ system cannot be fully exploited. Although several studies on improving the strength and toughness of the materials used in cantilevers have been carried out, these materials have not been widely used in CDQ systems because of their complicated preparation processes, high cost, and low toughness [2–5].

In our previous study [6], a mullite-silicon carbide refractory with high strength and excellent thermal shock resistance was successfully fabricated for use in cantilevers *via* the formation of AlN whiskers *in situ* in the matrix using metallic Al powder and circulating gas in a CDQ furnace. However, the main drawback in this case was the high formation temperature of the AlN whiskers (approximately 1000 °C), which exceeds the temperature at the bottom of the cantilever (the temperatures at the top and bottom of the cantilever are approximately 1000 and 850 °C, respectively). Many researchers have reported the rapid and effective synthesis of AlN whiskers by using catalysts [7–9], while a few studies have reported the effect of these catalysts on the formation temperature of the whiskers. Zhua et al. [10] synthesized mullite ceramic whiskers by a facile solid-state reaction, using kaolin and $Al(OH)_3$ as the raw materials and MoO_3 as the catalyst. They found that the initial temperature of the mullitization reaction decreased by approximately 200 °C upon the addition of the catalyst. Dang et al. [11] synthesized one-dimensional AlN whiskers using the cobalt oxide catalyst-assisted carbothermal reduction method. They discovered that the reaction started at a lower temperature in the presence of a catalyst; the temperature for 100% transformation of Al_2O_3 was 1500 °C and 1700 °C in the presence and absence of the catalyst, respectively. Liu et al. [12] achieved complete conversion from Si to Si_3N_4 after nitridation at 1400 °C for 2 h using Fe_2O_3 nanoparticles as the catalyst, and the conditions for the catalyst-assisted reaction were milder than those for the reaction without the catalyst (1450 °C and long hours). However, studies on the *in situ* formation of AlN whiskers in a mullite-silicon carbide refractory at temperatures below 1000 °C have not been reported.

In the present work, we added catalysts and metallic Al powder simultaneously to the refractory raw materials in order to obtain AlN whiskers *in situ* in mullite-silicon carbide refractories under the simulated conditions of a CDQ furnace. The formation temperature of the AlN whiskers and its influence on the properties of the refractory were

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https://doi.org/10.1016/j.ceramint.2017.12.162
Received 21 November 2017; Received in revised form 16 December 2017; Accepted 22 December 2017

studied.

2. Materials and methods

2.1. Raw materials and preparation of samples

Sintered mullite (particle sizes: 3–5 mm, 1–3 mm, and 0–1 mm; Zibo Luhong Woersen Ceramic Co., Ltd., Shandong, China) and SiC (particle sizes: 1–3 mm, 0–1 mm; Henan Ming Maite New Material Technology Co., Ltd., Henan, China) were selected as refractory aggregates. Sintered mullite powder (0.074 mm; Zibo Luhong Woersen Ceramic Co., Ltd., Shandong, China), SiC powder (0.074 mm; Ming Maite New Material Technology Co., Ltd., Henan, China), α-Al_2O_3 micropowder (1–5 μm; Kaifeng Special Refractory Co., Ltd., Henan, China), fused silica powder (0.074 mm; Xinyi Wanhe mining Co., Ltd., Jiangsu, China), and micro-silica (Elkem International Trade Co., Ltd., Shanghai, China) were chosen as matrix materials. A liquid thermosetting phenolic resin (36 wt%; Wuhan Lifa Chemical Co., Ltd., Hubei, China) was used as the binder. Metallic Al powder (d_{50} = 38 μm; Changsha Tianjiu Metallic Material Co., Ltd., Hunan, China) was used as the additive.

Many studies have demonstrated that nanoscale Fe is an effective catalyst for whiskers formation [13–15]. Hence, we selected nanoscale Fe powder (Fe, > 99.9 wt%; d_{50} = 50 nm; Shanghai ST-NANO technology Co., Ltd., Shanghai, China) as the catalyst in our study. The main constituents of Si_3N_4-Fe are Si_3N_4 and free Fe. It has been verified that the strength of mullite-SiC refractories can be improved by adding Si_3N_4 to the raw materials [4]. In order to study the catalytic effect of free Fe, we added Si_3N_4-Fe powder (Si_3N_4, 84.56 wt%; Fe, 12.44 wt%; Al_2O_3, 1.47 wt%; CaO, 0.52 wt%; d_{50} = 0.074 mm; Anyang Dingxing Metallurgical Refractories Co., Ltd., Henan, China) as a comparative catalyst. The compositions of the prepared samples are listed in Table 1.

The raw materials were homogenously mixed in a standard mortar mixer (Eirich R201-x02, Germany) and then pressed into 25 mm × 25 mm × 150 mm and Φ50 mm × 50 mm samples at 100 MPa. The pressed samples were dried at 200 °C for 24 h and then fired under nitrogen flow (over 98 wt% purity) for 8 h at 600, 850, 1000, and 1200 °C, respectively.

2.2. Testing and characterization methods

The apparent porosity (AP) and bulk density (BD) of the samples were measured according to Archimedes' principle using kerosene as the medium. The cold crushing strength (CCS) for the Φ50 mm × 50 mm samples and cold modulus of rupture (CMOR) for the 25 mm × 25 mm × 150 mm samples were measured at 20 °C using a pressure testing machine with an electronic digital control system (LM-02, Longsheng Test Facility Co. Ltd., China).

The hot modulus of rupture (HMOR) of the 25 mm × 25 mm × 150 mm samples was measured under a nitrogen atmosphere. The samples were heated to 1000 °C at the rate of 5 °C/min and maintained at this temperature for 0.5 h; then, the HOMR was measured by three-point bending tests. The thermal shock resistance of the 25 mm × 25 mm × 150 mm samples was evaluated using the air-cooling method, between 1000 °C and 20 °C. After heating at 1000 °C for 0.5 h, the samples were directly taken out of the furnace and cooled under compressed air (with an outlet pressure of 0.1 MPa and temperature of 20 °C) for 5 min. This constitutes one thermal shock cycle. After five thermal shock cycles, the residual cold modulus of rupture ($CMOR_{TS}$) of the samples was measured. The retained CMOR ratio (η) was calculated using the equation $\eta = (CMOR_{TS}/CMOR) \times 100\%$.

The microstructures of the fractured surfaces were observed using a field-emission scanning electron microscope (FE-SEM; Nova Qsuanta 400) equipped with an energy-dispersive X-ray spectrometer (EDS, Phoenix, AMETEK Process Instruments).

The mechanical behavior was determined from the stress-deformation curves obtained in three-point bending tests at different temperatures under a reducing atmosphere in an electrical furnace containing Mo_2Si heating elements. Bar-shaped samples (25 mm × 25 mm × 150 mm) were used for the tests. The details of the test have been reported in our previous study [6].

Table 1
Compositions of samples.

Raw material		Contents (%)			
		Sample B0	Sample C0	Sample C1	Sample C2
Sintered mullite		50	50	50	50
Silicon carbide		38	32	32	32
α-Al_2O_3 micro powder		7	7	7	7
Micro silica		3	3	3	3
Fused silica		2	2	2	2
Thermosetting resin (external)		4	4	4	4
Metal Al powder		0	6	6	6
Catalyst (external)	Nano iron powder	0	0	0.5	0
	Si_3N_4-Fe powder	0	0	0	0.5

3. Results and discussion

3.1. Effect of catalyst on microstructure and whisker-formation mechanism

The FESEM images of the microstructures of the samples at different temperatures are shown in Fig. 1. After heat treatment at 600 °C, the metallic state of the Al powder was preserved in sample C0, while in samples C1 and C2, thin AlN films were formed on the surface of the metallic Al powder. It is believed that the Al powder did not melt at the start of nitridation on the surface of the metallic Al powder, whereas the catalyst improved the reaction between Al and N_2 to form AlN films by decreasing the activation energy [11] and decreased the reaction temperature. From the fracture morphology, it was evident that the AlN films in sample C1 covered the surface of the metallic Al powder, but those in sample C2 detached from the surface, exposing the metallic Al powder. This may be attributed to the different catalytic effects of nanoscale Fe powder and Si_3N_4-Fe powder on the formation of AlN films.

When the nitriding temperature was increased to 850 °C, AlN was observed in all the samples, but its morphology differed: hexagonal facets in sample C0, hexagonal columns in sample C1, and whiskers (length 2–10 μm; diameter 5–100 nm) in sample C2. The crystalline columns in sample C1 can be regarded as the initial growth morphology of the whiskers. The formation temperature of the AlN whiskers was decreased by the addition of nanoscale Fe powder and Si_3N_4-Fe powder to the raw materials. The presence of droplets on the top of the whiskers, as shown in Fig. 1c-2) and c-3), indicated that the mechanism of AlN whisker formation changed from solid-gas (s-g) in sample C0 to solid-liquid-gas (s-l-g) in sample C2 [16,17].

As the temperature was increased to 1000 °C, AlN whiskers were formed in all the samples. The amount of whiskers formed in sample C0 was smaller than that formed in samples C1 and C2 because of the different reaction mechanisms. The differences in the amount and length of the whiskers between samples C1 and C2, as shown in Fig. 1b-3) and c-3), could be attributed to the different adsorption coefficients.

3.2. Effects of catalysts on physical properties

As shown in Fig. 2, the mass change ratios of all the samples were negative when the temperature was 600 °C, because of thermal decomposition and volatilization of the resin. When the temperature was increased above 850 °C, the mass change ratios became positive because of the formation of AlN in the samples, which was confirmed by the FESEM images in Fig. 1. After heat treatment at 850 °C under