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Original Article

Enhanced thermal shock resistance of low-carbon Al_2O_3-C refractories with direct CVD synthesis of nano carbon decorated oxides

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ABSTRACT

Novel low carbon Al_2O_3-C refractories were prepared through adopting chemical vapour deposition (CVD) synthesized nano carbon decorated Al_2O_3 powder. The phase compositions, microstructures, mechanical properties and thermal shock resistance of Al_2O_3-C refractories were characterized and evaluated. The results show that the morphologies of nano carbon composites are mainly dominated by the concentration of catalyst. Specifically, the growth of MWCNTs is preferred with a Ni^{2+} concentration at 0.1 mol/L, while higher concentrations e.g. 0.3 mol/L would stimulate the formation of nano-onion like carbon. With the introduction of nano carbon decorated Al_2O_3 additives, the residual strength after thermal shock can reach 12.4 MPa, which is much higher than the 2 wt% nano carbon black containing specimens (6.4 MPa). The enhanced thermal shock resistance should be attributed to that the nano onion-like carbon reduces the cohesion between the matrix and the Al_2O_3 particles and decreases the thermal expansion coefficient.

1. Introduction

Carbon containing refractories have served the steel making vessels in the last few decades. As one of them, Al_2O_3-C refractories were applied successfully in the slide gates due to their good thermal and chemical stability [1,2]. However, the high content of carbon in traditional Al_2O_3-C refractories (often comprise 5–8 wt% graphite) may not satisfy the state of the art in developing clean smelting technology and reducing the greenhouse gases emissions. Therefore, it is of great importance to prepare low-carbon containing Al_2O_3-C refractories. However, the thermal shock resistance would be challenged with reducing carbon content below 3 wt% directly.

Generally, the methods used in the prediction of thermal shock behavior were based largely on the work of Hasselman [3–5], which was conducted more than thirty years ago. They discussed the relationships between fracture stresses, fracture energies and the fracture behavior of brittle ceramics [6,7]. Based on their concepts, the decreasing of thermal expansion coefficient (CTE) and young's modulus, as well as the increasing of fracture energies should be feasible to improve the thermal shock resistance [8]. In addition to this theory, Bradt [9] also reported that the crack interactions with microstructure could influence the thermal shock resistance. They have revealed that the initial crack density increased with the increasing of mullite-zirconia aggregates, which have lower thermal expansion coefficient than the alumina matrix. Regarding this concept, Huger [10] et al. has highlighted that The CTE mismatch existing between andalusite aggregate and matrix induced the debonding at interfaces and microcracks in the matrix. This damage leaded to decreased thermal expansion and improved non-linear character of the stress-strain curves. In addition, one still can take advantages of the anisotropic dilation of andalusite to prepare microcracks [11]. Furthermore, they have designed the magnesia-spinel refractories accordingly. Due to the CTE mismatch between magnesia and spinel, microcracks could be found at the interfaces between matrix and particles [12]. Therefore, the newly designed refractories showed much better properties. Coincidentally, researchers have also found that the appropriate choose of aggregates can provide sufficient energy dissipation [13,14]. Besides, wedge splitting tests and digital image correlation were combined to better understand the specific mechanism [15,16]. Based on their investigations, a strain-to-rupture of refractories is considered as a key parameter for improving thermal shock resistance. Consequently, the investigation of the cracks propagation and the debonding between phases has been highlighted [17–19].

Inspired by these concepts, the microstructure design of the carbon

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containing refractories was intensively conducted for achieving better thermal shock resistance. For example, the introduction of more graphite could function as weak interfaces, inducing the cracks propagation [20]. However, this was not feasible to produce the low/ultra-low carbon containing refractories. Another feasible way was to employ a weak interface in the matrix through adding nano carbon particles [21,22]. As for the low-carbon containing refractories, the introductions of nano carbon black [23–27], MWCNTs [28,29], and graphene oxide nanosheets [30,31] etc. have been investigated in the last decade. In addition, the combination of nano additives exhibited good application potential [32]. However, the dispersion shortage and high cost of nano additives are still obstacles for industrial applications. Luo [33] et al. reported that the introduction of catalyst can stimulate the formation of *in-situ* MWCNTs and SiC whiskers during heat treatment and thereby enhance the Al_2O_3-C refractories significantly. Besides, our former work also revealed that dissolving of catalyst in resin binder could increase the strength considerably and coating catalyst on alumina powder would improve the thermal shock resistance [34]. Meanwhile, nano onion-like carbon could be also prepared with this method as reported by Zhu [35] et al. Although the above works demonstrated the prospects of nano carbon applications, the interface design should be further optimized. In fact, an alternative method can be imitated from MWCNTs enhanced alumina [36] and zirconia ceramics [37], where the MWCNTs were directly grown on raw powders through CVD. With this method, the dispersion of MWCNTs and its content can be designed according to requirement.

Therefore, the present work mainly devoted to optimize the interfaces between oxides and nano carbon particles, which can take advantages of the aforementioned interface debonding effects and energy dissipation mechanisms during thermal shock. The CVD process was employed to prepare nano carbon decorated alumina powder, where the nano carbon composites were mainly MWCNTs and nano onion-like carbon. The morphologies and contents of nano carbon were designed through adjusting the concentration of catalyst. Afterwards, the microstructure evolutions of nano carbon in Al_2O_3-C matrixes were investigated. Afterwards, the effects of pre-synthesized nano carbon decorated Al_2O_3 powder on the mechanical properties and thermal shock resistance of low-carbon Al_2O_3-C refractories were comparatively addressed. It is revealed that MWCNTs and nano onion-like carbon can be obtained from CVD process depending on the catalyst concentration. Additionally, the designed low-carbon Al_2O_3-C refractories present much better thermal shock resistance mainly attributes to more energy dissipations (including debonding and cracks propagation) and the decreased CTE.

2. Experimental

2.1. Preparation of nano carbon composites@Al_2O_3 powder

Firstly, the reactive alumina powder (~2 μm, 98 wt% Al_2O_3, Qingdao Almatis Premium Alumina Co. Ltd., China) needed for refractories batches was impregnated in $Ni(NO_3)_2{\cdot}6H_2O$ solution with different Ni^{2+} concentrations (0.1, 0.2, and 0.3 mol/L) and stirred for 15 min accompanied with sonication. Then the slurries were filtrated and dried at 80 ℃ for 12 h to obtain the catalyst loaded alumina powders. Afterwards, the alumina powders were put into a horizontal quartz tube (100 mm in diameter and 750 mm in length) heated with a tube furnace. It is worth noting that the quartz tube was equipped with a rotary device, which allowed a homogeneous reaction condition. In the beginning, N_2 (500ml/min) was adopted to eliminate the initial air for 30 min. Afterwards, N_2 tube was inserted into ethanol, which has already been maintained at 80 ℃ in a water bath, to feed the ethanol vapor together with N_2. The furnace was heated to 1000 ℃ at a heating rate of 10 ℃/min and hold at this temperature for 3h. After the deposition, ethanol inlet was terminated and the flow of N_2 was adjusted to 200 ml/min until the samples were cooled to room temperature. Additionally, the rotary speed was set at 5 r/min during the whole experiment. The acquired nano carbon composites@Al_2O_3 powders were named as Al_2O_3-Ni-0.1, Al_2O_3-Ni-0.2 and Al_2O_3-Ni-0.3, corresponding to the Ni^{2+} concentrations.

2.2. Preparation of Al_2O_3-C matrixes

In order to better investigate the structure evolutions of nano carbon composites under elevated temperatures, the Al_2O_3-C matrixes with synthesized powders and silicon powder (45 μm, 98.47 wt% Si, Anyang, China) were prepared. In this experiment, a mass ratio of nano carbon@Al_2O_3:Si was set as 10:2. Besides, no alumina aggregates were added because they showed no influence on the structure evolution of MWCNTs [38]. The raw materials were mixed in ethanol by means of planetary ball milling for 4h at a speed of 300 r/min. Afterwards, the mixture was dried at 80 ℃ for 24 h, and then cold pressed into specimens of Φ20 mm*5 mm at 65 MPa. Finally, the as-prepared Al_2O_3-C matrix specimens were coked at 1200 and 1400 ℃ in a sagger filled with coke grit for 3h, respectively. A heating rate of 5 ℃/min was applied before 1000 ℃ and 2 ℃/min above 1000 ℃.

2.3. Preparation of Al_2O_3-C refractories

The raw materials used for Al_2O_3-C refractories were tabular alumina (3.0–1.0, 1.0–0.5, 0.6–0.2, 0.3–0 mm, ~45 μm, ~20 μm, 98 wt% Al_2O_3, Qingdao Almatis Premium Alumina Co. Ltd., China), the synthesized nano carbon@Al_2O_3 powder, nano carbon black (20–30 nm, 99.5 wt% fixed carbon, Wuhan Cobo New Materials Co. Ltd., China) and silicon powder (45 μm, 98.47 wt% Si, Anyang, China). Additionally, thermosetting phenolic resin (liquid, ≥40 wt% fixed carbon, Wuhan Lifa Chemistry & Industry Co., Ltd., China) was added as a binder. There were three batches designed in the present work based on the obtained nano carbon composites@Al_2O_3 powders. The silicon content was set as 4 wt% and 1 wt% nano carbon black was introduced in all batches.

For a probable homogeneous distribution of nano carbon sources in the matrix, the fine powders were pre-mixed for 10 min firstly in a Hobart mixer, and then the aggregates were mixed for 3–5 min before the binder was introduced. After 5 min mixing of aggregates with binder, the pre-mixed fine powders were added and the mixing process held for another 30 min. The mixtures were then cold pressed into specimens of 25 mm × 25 mm × 140 mm at 150 MPa and cured at 180 ℃ for 24 h. Finally, the as-prepared Al2O3-C specimens were coked at 1000–1400 ℃ in a sagger filled with coke grit for 3 h. The heating profile was kept the same with the above.

2.4. Testing and characterization

The phase compositions of the specimens were analyzed by X-ray diffraction (XRD, x'Pert Pro, Philips, Netherlands). Microstructures of the specimens were observed by a field emission scanning electron microscope (FESEM, Nova 400 NanoSEM, FEI Company, USA) and transmission electron microscopy (TEM-2100 UHR STEM/EDS JEOL), both of them were equipped with energy dispersive X-ray spectroscope (EDS, INCA IE 350 PentaFET X-3, Oxford, UK). Thermogravimetry-differential scanning calorimetry (TG-DSC, STA449, NETZSCH, Germany) was employed to evaluate the deposited carbon content during CVD process. The Raman spectra of prepared powders were detected with a high-resolution dispersive Raman spectrometer system (Horiba-Jobin YvonLabRam HR) equipped with a confocal microscope (Olympus BX-30) and a notch filter (532 nm). Flexural strengths of coked specimens were measured by the three-point bending test at ambient temperature with a span of 80 mm and a loading rate of 0.5 mm/min using an electronic digital control system (EDC 120, DOLI Company, Germany). The thermal shock tests for the Al_2O_3-C specimens after coking at 1400 ℃ were carried out. Firstly, the specimens