Applied Clay Science 101 (2014) 94–99

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Phase transformation of coal gangue by aluminothermic reduction nitridation: Influence of sintering temperature and aluminum content

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A R T I C L E I N F O

Article history:
Received 30 March 2013
Received in revised form 9 July 2014
Accepted 20 July 2014
Available online 10 August 2014

Keywords:
Coal gangue utilization
High-temperature kaolinite composite
Aluminothermic reduction nitridation
β-SiAlON/corundum products

A B S T R A C T

The effect of sintering temperature and aluminum content on the phase transformation of coal gangue by aluminothermic reduction nitridation (ARN) was investigated. The process was carried out in flowing N_2 within the temperature range of 1400–1500 °C and holding time of 4 h. The results showed that temperature and Al content were two essential factors determining the nitridation of coal gangue and the phase yields of nitrided products. Kaolinite, the main mineralogical phase of coal gangue, was transformed into high-temperature composites containing β-SiAlON, corundum and $Al_6O_3N_4$ by ARN at 1400–1500 °C. The products consisted of globular β-SiAlON/corundum particles and continuous SiAlON fibers. The transformation provided a feasible mean of dealing with coal gangue for high-temperature utilization.

1. Introduction

Coal gangue is a kind of by-product which was produced during mining, washing and selection of coal. Statistics show that 0.2 billion tonnes of coal gangue is annually produced and the accumulative reserve has already reached 3.8 billion tonnes in China (C. Li et al., 2010), which causes pressing environmental problems in provinces such as Inner Mongolia, Shanxi, Liaoning and Henan in North China (Huang et al., 2006). The huge amount of reserve is also a most important economic concern. Efforts have been made to the use of coal gangue for different purposes (Han and Li, 2005; Ji et al., 2013; D.X. Li et al., 2006; Yang et al., 2012). For example, the coal gangue, especially these with less impurities, has been used in the manufacture of building products (pottery, cement, etc.) and refractories (mullite, SiC, etc.).

SiAlONs are a family of oxynitride materials that have wide range of applications owing to excellent properties such as high strength retention at elevated temperatures, high decomposition temperature, high wear-resistance, good resistance to erosion and thermal shock, which attract great interests for high temperature and mechanical applications (Huang et al., 2012). The carbothermal reduction nitridation (CRN) method is one of the most common and widely investigated approaches to transform coal gangue into SiAlON powders (Zhang, 2004). The CRN of coal gangue could obtain high temperature phases including β-SiAlON, O′-SiAlON, X-SiAlON, Si_2N_2O, SiC, Si_3N_4, and residual carbon, as revealed in literatures (Bahramian and Kokabi, 2011; Zhang, 2004). However, when used for applications with limited carbon, the residual carbon exsisting in the CRNed products of coal gangue must be removed, generally by heat treatment at 600–800 °C in the air for several hours. This complicates the procedure, increases the cost and causes possible oxidation to SiAlONs. Thus, to transform coal gangue into SiAlON composites using Al as reductant is becoming an alternative approach.

Aluminum has been used as a reductant in vacuum or under N_2 atmosphere, to prepare refractories, metal–ceramics, and nanocomposites such as Spinel–Corundum–Sialon (Huang et al., 2014), $MgAl_2O_4$–Ti(C,N) (Omid et al., 2013), $Al_8B_4C_7$ (Gao et al., 2012), β-SiAlON–AlN polytypoid (J.J. Li et al., 2010), and $MgAl_2O_4$–TiN (Li et al., 2005, 2007). They are known as the aluminothermic reaction (AR) and aluminothermic reduction nitridation (ARN) process, respectively. The cost-effective and free-carbon removal process of ARN makes it more attractive to synthesize SiAlONs, compared with the traditional solid state synthesis approach and the CRN approach. In the mid 1970s, Umebayashi and Kobayashi (1975) transformed volcanic ash into β-SiAlON in N_2 at 1300–1400 °C, using Al powder as the reductant. Decades later, Albano et al. (1992) investigated the formation mechanism of β-SiAlON in SiO_2–Al–N_2 system up to 1440 °C, revealing that major β-SiAlON was obtained with X-SiAlON and mullite as minor constituents. Afterward, Mazzoni and Aglietti (1997a,b, 1998, 1999, 2000) and Mazzoni (1996) systematically investigated the phase evolution of diatomite, bentonite, andalusite, and mullite by ARN process up to 1650 °C and obtained β-SiAlON, α-Al_2O_3 and Sialon polytypoid composites. More recently, Y.W. Li et al. (2006)

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http://dx.doi.org/10.1016/j.clay.2014.07.023
0169-1317/

reported the synthesis of 21R AlN-polytypoids, α-Al_2O_3 and β-SiAlON composites from ultrafine SiO_2 and Al in N_2 at 1400–1600 °C. The aforementioned results suggest that aluminosilicate clays and clay minerals can be transformed into SiAlON composites by ARN. Coal gangue is a kind of by-product mainly consisting of SiO_2 and Al_2O_3, so it is probably another candidate for preparing SiAlONs. Compared with the referred clays and mullite, coal gangue is more abundant and cost-effective. However, to the best of our knowledge, limited fundamental research on the transformation of coal gangue into SiAlON and corundum composites by ARN has been reported.

In this paper, coal gangue was treated with the aluminothermic reduction nitridation method and the effects of sintering temperature (1400, 1450 and 1500 °C) and Al addition (lack 10 wt.% of theoretical quantity, theoretical quantity, excess 10 wt.% and 30 wt.% of theoretical quantity) on the phase behavior and microstructure were studied. Furthermore, the reaction mechanism of coal gangue by ARN was also preliminarily discussed.

2. Experimental

The coal gangue rock was collected from Junggar Opencast mine, Inner Mongolia, Northwest China. The as-received coal gangue was crushed, ground, and passed through a 150 mesh sieve. Its chemical components are given in Table 1. Aluminum (Al) powder (75–150 μm, purity > 99.9%, Beijing Jingwen Chemical Reagents Company, China) was used as the reductant. Pre-calcination of coal gangue at 800 °C for 2 h in the air was conducted to get rid of carbonaceous components prior to the ARN process. As shown in Fig. 1, the main mineralogical phase of coal gangue was identified to be kaolinite via the XRD analysis. β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$, $0 < z \leq 4.2$) phase was designed with $z = 3$ (i.e., $Si_3Al_3O_3N_5$) and the nitridation of the pre-heated coal gangue was considered to proceed as Eq. (1):

$$3(Al_2O_3 \cdot 2SiO_2) + 10Al + 5N_2 = 2Si_3Al_3O_3N_5 + 5Al_2O_3. \quad (1)$$

A series amount of Al powder (lack 10 wt.% of theoretical quantity, theoretical quantity, excess 10 wt.% and 30 wt.% of theoretical quantity) were mixed with the pre-heated coal gangue, denoted as sample S1, S2, S3, and S4, respectively. Here, the theoretical stoichiometry is defined by the proportion of pre-heated coal gangue and Al based on a principle of complete nitridation of SiO_2 and Al_2O_3 in the pre-heated coal gangue; the theoretical Al addition refers to the amount required in the complete reaction Eq. (1). Then, excessive Al additions are calculated based on the theoretical value. The powders were dry-mixed using a planetary mill for 6 h in a polyurethane jar with agate balls as the milling media (ball-to-powder = 4:1 w/w). Afterward, the powder mixtures were shaped into bar specimen (~5 mm × 8 mm × 40 mm) and pressed under 200 MPa by cold isostatic compaction. The green bodies were placed in a graphite crucible and nitrided in N_2 (purity 99.99 wt.%) with a furnace gas pressure of ~0.12 MPa and a flowing rate range of 1.5–3 L/min. The furnace was heated to 1000 °C at a rate of 10 °C/min, and elevated to the final temperature (1400, 1450, and 1550 °C) at a rate of 5 °C/min, maintaining for 4 h. Finally, the sintered samples were furnace-cooled to room temperature.

Phase identification of sintered pellets crushed was performed by powder X-ray diffractometry (XRD; XD-3, Purkinje General Instrument Co., Ltd., China) using Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å) with a step of 0.02° (2θ) and a scanning rate of 8° min^{-1}. The microstructure and

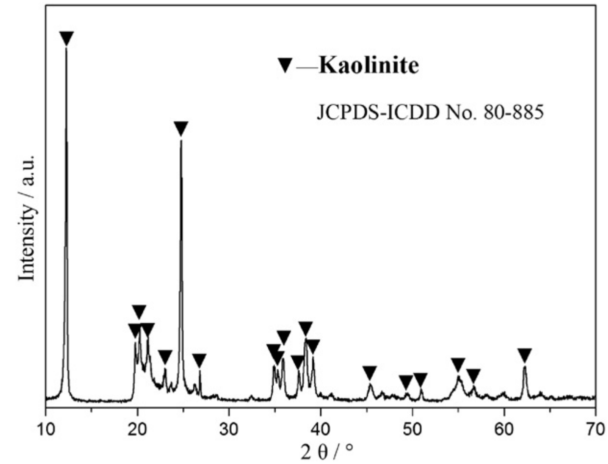

Fig. 1. The XRD pattern of raw coal gangue.

morphologies were observed by scanning electron microscopy (SEM; JEM-6460LV, Japan Electron Optics Laboratory Co., Ltd., Japan) equipped with an energy dispersive spectroscopy detector (EDS; OXFORD INCA X-Sight, UK). The samples were coated with gold using a sputter coater to increase conductivity prior to SEM characterization.

Moreover, a method proposed by Y.W. Li et al. (2006) was utilized to quasi-quantitatively estimate phases appeared in the products, which was based on diffraction peak intensities of the phase to be characterized. Specifically, β-SiAlON (wt.%) in the products was calculated according to Eq. (2) by using the intensities of reflection lines of [$d_{(020)} = 3.32$] for $Si_3Al_3O_3N_5$, [$d_{(012)} = 3.48$] for α-Al_2O_3 and [$d_{(101)} = 2.62$] for $Al_6O_3N_4$. Similar equations were used to estimate the relative contents of α-Al_2O_3 and $Al_6O_3N_4$ phases.

$$\beta\text{-SiAlON wt.\%} = I_{\beta\text{-SiAlON}} / \left(I_{\beta\text{-SiAlON}} + I_{\alpha\text{-}Al_2O_3} + I_{Al_6O_3N_4} \right) \times 100\%. \quad (2)$$

3. Results and discussion

3.1. Effect of temperature and Al content on phase behavior of coal gangue

XRD patterns of sample S2 (reductant Al of theoretical quantity) and S4 (reductant Al excess 30 wt.% of theoretical quantity) ARNed at 1400, 1450 and 1550 °C for 4 h are shown in Fig. 2. The main phases of the products of S2 were β-SiAlON (with z = 3) and corundum at these temperatures (Fig. 2a), which were well matching with the nitridation design of the coal gangue–Al mixture (shown in Eq. (1)). Moreover, for S4 with excessive Al addition, diffraction peaks of $Al_6O_3N_4$ were detected at 1400 °C, and minor $Al_6O_3N_4$ was obtained in final products when the temperature was elevated to 1500 °C (Fig. 2b). Thus, the sintering temperature has a great influence on phase composition of samples. The formation mechanism of equiaxed β-SiAlON particles can be readily explained by the solid–solid diffusion reaction between Si_3N_4, Al_2O_3 and AlN (Navrotsky et al., 1997).

Besides the oxynitride and corundum products, the diffraction peaks of mullite, a primary product of fired kaolinite, were also detected in the XRD pattern of sample S1 with reductant Al lack 10 wt.% of theoretical quantity sintered at 1400 °C (shown in Fig. 3). This phenomenon

Table 1
Chemical composition of the raw coal gangue.

Component (wt.%)												
SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O^-	LOI[a]
45.55	0.37	37.56	0.10	0.13	0.01	0.43	0.44	0.16	0.21	0.03	0.55	15.30

[a] Loss on ignition.