Synthesis of ZrN–Si3N4 composite powders from zircon and quartz by carbothermal reduction and nitridation

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A R T I C L E   I N F O

Article history:
Received 1 March 2013
Received in revised form 4 May 2013
Accepted 22 June 2013
Available online 1 July 2013

Keywords:
ZrN–Si3N4 composite powders
Zircon
Quartz
Carbothermal reduction nitridation

A B S T R A C T

ZrN–Si3N4 composite powders were synthesised from natural zircon and quartz via carbothermal reduction and nitridation reaction. The effects of various raw material compositions and heating temperatures on phase transformation and product morphologies under flowing nitrogen atmosphere were investigated by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. The phase equilibrium relationships of the ZrO2–SiO2–C–N2 system at different heating temperatures were also investigated based on the thermodynamic analysis. Products with different phase compositions and morphologies were obtained at different conditions. The products were composed of ZrN, β-Si3N4 and a small amount of c-ZrO2 by carbothermal reduction and nitridation of zircon with less than 20 wt.% quartz. With 30 wt.% quartz, granular ZrN as well as columnar and acicular β-Si3N4 were detected in the products. With 40 wt.% or 50 wt.% quartz, the products consisted of ZrN, β-Si3N4, Si3N4-0, c-ZrO2 and m-ZrO2. The optimum quartz content for synthesizing ZrN–Si3N4 composite powders was 30 wt.%. At heating temperatures below 1600 °C, the products were composed of ZrN, β-Si3N4, β-SiC, Si3N4-0, m-ZrO2 and c-ZrO2.

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1. Introduction

Zirconium nitride (ZrN) has been widely used in industries because of its high melting point, strength, toughness, good wear resistance, good electrical conductivity and low-temperature superconductivity [1,2]. Silicon nitride (Si3N4) ceramics are advanced materials that meet the requirements of mechanical, electronic, decorative, high-temperature industry and microwave-transparent applications because of their excellent properties, such as chemical stability, high-temperature resistance, wear resistance, high modulus of elasticity, dielectric properties, low thermal expansion and large thermal conductivity [3–5]. ZrN–Si3N4 composites can meet the requirements of high temperature, high strength and mechanical erosion resistance. According to the results of Ade and Haußelt [6], ZrN/Si3N4 nanolayers are deposited in a multitarget magnetron sputtering system and the films’ hardness is markedly enhanced to its maximum value of 33GPa. Zircon is one of the vital zirconium neosilicate minerals in nature. The crystal structure of zircon is made of [SiO4] tetrahedron and [ZrO8] trigonododecahedron [8]. The [SiO4] tetrahedron can be transformed into SiC or Si3N4 materials, and the [ZrO8] trigonododecahedron can be changed into ZrO2 or ZrN materials via carbothermal reduction (CR) or CR and nitridation (CRN). Zircon is one of the fundamental raw materials for manufacturing many vital industrial zirconium compounds, such as ZrO2, ZrN and ZrB2.

In recent years, zircon has been used as a main raw material to synthesise high-temperature composites, such as ZrO2–SiC, ZrN–sialon and ZrC–SiC [9–12]. CRN, which has high efficiency, wide raw material sources, low cost, massive production and controllability [13–15], is a vital method for the synthesis of inorganic powder materials, especially in the field of silicate mineral transformation. CRN was employed to prepare β-sialon powders from zeolites and to synthesise high-purity Si3N4 powders from diatomite [16,14]. According to our previous study, the optimal heating temperature for the CRN of zircon is 1600 °C and the main phases are ZrN and Si3N4, with a small amount of c-ZrO2 [17]. The amount of Si3N4 was significantly lower than that of ZrN because of the running off of Si element as volatilised intermediate product (SiO). Quartz can be used as a starting material to obtain effectively higher amounts of Si3N4 in the products and to optimise the mass ratio of Si3N4 to ZrN in the products. This method can provide an experimental basis for the synthesis of ZrN–Si3N4 composite powders from zircon and quartz.

In this work, zircon and quartz were used as the main raw materials for the synthesis of ZrN–Si3N4 composite powders by CRN. The equilibrium relationships of the condensed phases in the ZrO2–SiO2–C–N2 system were analysed. The effects of quartz and heating temperature on the phase compositions and morphologies of the products were also investigated. The ZrN–Si3N4 composite powders

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http://dx.doi.org/10.1016/j.powtec.2013.06.029

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can be used in high-temperature industries. Our method can also provide a basis for improving the use of zircon and quartz.

2. Materials and methods

2.1. Material preparation

Zircon was produced by Australian Winner International Exhibition Pty Ltd. ZrSiO₄ content reached 98.8 wt.%. The chemical composition of zircon was determined through X-ray fluorescence. The results are shown in Table 1. Quartz was used as another raw material, and its chemical compositions in mass fraction were 97.8% SiO₂, 0.63% Al₂O₃, 0.33% Fe₂O₃ and 0.08% CaO. Carbon coke (dₐ₀ = 38 μm) was chosen as reductant, and the carbon content reached 80 wt.%. Nitrogen purity reached 99%. According to Eq. (1), the mass ratio between zircon and coke was designed to form ZrN–Si₃N₄ composite powders, and the component was assigned as A1. Based on this component, five more components with different amounts of natural quartz (10, 20, 30, 40 and 50 wt.%) were denoted as A2, A3, A4, A5 and A6, respectively. Carbon coke for the CRN of quartz was added based on Eq. (2).

\[ 6ZrSiO_4 + 24C + 7N_2 = 6ZrN + 2Si_3N_4 + 24CO \] (1)

\[ 3SiO_2 + 3C + 2N_2 = Si_3N_4 + 6CO \] (2)

The raw materials were weighed in terms of the stoichiometric amounts. The materials were fully mixed by ball milling for 6 h using alumina balls with different diameters as grinding medium and distilled water as milling solvent. The mixture was dried in a drying oven at 105 °C for 12 h. After being ground and sieved at 150 mesh, the powder mixtures were pressed at 100 MPa into the green samples with the size of Φ 20 mm × 10 mm. The green samples were dried at 70 °C for 24 h and then heated in a high-temperature atmosphere furnace at 1450, 1500, 1550 and 1600 °C for 4 h in a 0.13 MPa flowing nitrogen environment. The samples were stored in a graphite crucible.

After reaching the desired heating temperature and soaking time, the system was cooled to room temperature under nitrogen atmosphere.

2.2. Characterisation

The phase transformations of the products were analysed by a D/max rA X-ray diffractometer (Cu target, Kα1 radiation, λ = 1.5406 Å; Rigaku Corporation, Japan). The morphologies of the products were characterised by scanning electronic microscopy (JEOL, Japan). The micro-area compositions of the products were studied by energy dispersive spectroscopy (EDS; INCAX-Sigh EDS).

3. Results and discussion

3.1. Effects of various raw material compositions on the phase composition and micro-morphology of the products

The phase compositions of the products with different amounts of natural quartz are shown in Fig. 1. ZrN was the main phase in the products when the amount of quartz ranged from 0 wt.% to 50 wt.%, respectively. Small amounts of β-Si₃N₄ and c-ZrO₂ (cubic zirconia) were detected in the products when the amount of quartz in the raw materials ranged from 0 wt.% to 20 wt.%. The diffraction intensities of β-Si₃N₄ phase were enhanced significantly, and the diffraction peaks of c-ZrO₂ disappeared in the products with 30 wt.% natural quartz.

The results show that both zircon and quartz were nitried completely. When the amount of quartz was increased to 40 wt.% or 50 wt.%, ZrN, β-Si₃N₄, Si₃N₂O, m-ZrO₂ (monoclinic zirconia) and c-ZrO₂ phases were found in the products. In the present study, Si₃N₂O, m-ZrO₂ and c-ZrO₂ phases appeared in samples A5 and A6 because of the incomplete nitridation of SiO₂ and ZrO₂ in CRN. This result illustrates that increasing the amount of quartz in raw materials can compensate for the loss of Si element because of the volatilisation of the intermediate product SiO and can improve the nitridation of ZrO₂ to some extent. However, an excessive amount of quartz led incomplete nitridation of zircon and quartz and was harmful to the synthesis of ZrN–Si₃N₄ composite powders.

The morphologies of the products with different amounts of quartz by CRN at 1600 °C are outlined in Fig. 2. Granular ZrN and columnar β-Si₃N₄ were the main phases in the products from zircon and quartz via CRN at 1600 °C for 4 h. Granular ZrN was the major phase in the products when quartz was absent in the raw materials. With increasing quartz amount, β-Si₃N₄ was changed from short columnar to long columnar and then to acicular. The particle boundaries of β-Si₃N₄ were clear, and the content of β-Si₃N₄ increased compared with that in Fig. 2a. This result indicates that adding a certain proportion of quartz can promote the growth and development of β-Si₃N₄ in the products.

3.2. Effect of heating temperature on the phase composition and micro-morphology of the products

The effects of heating temperatures on the phase compositions of the products with 30 wt.% quartz are described in Fig. 3. At 1450 °C, the products were mainly composed of Si₃N₂O, m-ZrO₂ and c-ZrO₂ phases. The diffraction peaks of ZrN were observable, but their intensities were weak. In addition, the diffraction peaks of Si₃N₂O phase were hard to detect in the products. This result indicates that the nitridation of zircon and quartz was poor and that higher heating temperature was needed for ideal nitridation. When heating temperature rose to 1550 °C, Si₃N₂O phase vanished, and the diffraction intensities of m-ZrO₂ and c-ZrO₂ declined significantly. Furthermore, the diffraction intensities of ZrN increased sharply. ZrN became the main phase in the products and β-Si₃N₄ phase was observed. Elevating heating temperature improved the nitridation of zircon and quartz, whereas a higher heating temperature was required to transform ZrO₂ into ZrN completely. The products only consisted of ZrN and β-Si₃N₄.

Table 1

<table>
<thead>
<tr>
<th>Oxide name</th>
<th>ZrO₂</th>
<th>HfO₂</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Y₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>TiO₂</th>
<th>Cr₂O₃</th>
</tr>
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<tr>
<td>Percentage/wt.%</td>
<td>62.63</td>
<td>2.72</td>
<td>33.17</td>
<td>0.93</td>
<td>0.21</td>
<td>0.12</td>
<td>0.09</td>
<td>0.08</td>
<td>0.05</td>
</tr>
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</table>
when the heating temperature was 1600 °C, indicating that zircon and quartz both had perfect nitridation with a higher heating temperature. The analyses show that the optimal heating temperature was 1600 °C for the synthesis of ZrN–Si3N4 composite powders from zircon and quartz by CRN.

The micrographs of the products with 30 wt.% quartz at 1550 and 1600 °C are shown in Figs. 4a to c, respectively. Granular ZrN and columnar β-Si3N4 were observed, and the particle boundaries were clear when heating temperatures were 1550 and 1600 °C. After 4 h at 1600 °C, acicular structures were found in the products. Combined with the EDS analysis of area A in Fig. 4c, the acicular structural material was β-Si3N4. Characteristic droplets were observed at the tips of the crystal. These droplets may have resulted from the iron impurities from the raw materials.

3.3. Thermodynamic analysis of CRN of zircon and quartz

The complex ZrO2–SiO2–C–N2 system was formed during the CRN of zircon and quartz. The standard Gibbs free energies of the formation of main compounds in the system are listed in Table 2. The possible reactions are given in Eqs. (3) to (8), and their standard Gibbs free energies are shown in Table 3.

\[
\begin{align*}
\text{ZrSiO}_4(s) &\rightarrow \text{Si}_2\text{O}_2(s) + \text{ZrO}_2(s) \tag{3} \\
\text{SiO}_2(s) + 3\text{C}(s) &\rightarrow \text{SiC}(s) + 2\text{CO}(g) \tag{4} \\
2\text{SiO}_2(s) + 3\text{C}(s) + \text{N}_2(g) &\rightarrow \text{Si}_2\text{N}_2\text{O}(s) + 3\text{CO}(g) \tag{5} \\
3\text{SiO}_2(s) + 6\text{C}(s) + 2\text{N}_2(g) &\rightarrow 3\text{Si}_3\text{N}_4(s) + 6\text{CO}(g) \tag{6} \\
2\text{ZrO}_2(s) + 4\text{C}(s) + \text{N}_2(g) &\rightarrow 2\text{ZrN}(s) + 4\text{CO}(g) \tag{7} \\
6\text{ZrSiO}_4(s) + 24\text{C}(s) + 7\text{N}_2(g) &\rightarrow 6\text{ZrN}(s) + 2\text{Si}_3\text{N}_4(s) + 24\text{CO}(g) \tag{8}
\end{align*}
\]

As shown in Table 2, the Gibbs free energies of reactions (4) to (7) were calculated. The results are shown in Table 3. When $p_{N_2} = 0.13\text{MPa}$ (where $p_{N_2}$ is the partial pressure of $N_2$), the relationship between the partial pressure of CO gas and heating temperature was achieved when the reactions were balanced. The equilibrium relationship curves plotted as $ln{p_{CO}}$ with $\frac{1}{T}$ (where $p_{CO}$ represents the partial pressure of CO, $p^0$ represents the standard atmospheric pressure and $T$ represents heating temperature) are shown in Fig. 5.

The stable region diagram of each phase in the ZrO2–SiO2–C–N2 system was drawn according to Eqs. (4) to (8). Their thermodynamic data are shown in Fig. 5. When the partial pressure of CO gas was kept constant and heating temperature was increased, SiO2 was changed into Si2N2O via Eq. 4. Subsequently, Si2N2O reacted with C and N2, and then finally completely transformed into SiC and Si3N4. Changing ZrO2 into ZrN by nitridation was helpful because of increasing heating.
temperature. When the heating temperature was constant, the stability domains of each phase changed from ZrO$_2$–SiO$_2$–C to ZrN–Si$_3$N$_4$–SiC–C with continuously decreasing $p_{CO}$. ZrN, Si$_3$N$_4$ and SiC can be found in the products by controlling the partial pressure of CO gas and heating temperature in furnace.

4. Conclusions

ZrN–Si$_3$N$_4$ composite powders were successfully synthesised from zircon and quartz via CRN. The final phase compositions were strongly dependent on the various raw material compositions and heating temperatures. The optimum amount of quartz for the synthesis of ZrN–Si$_3$N$_4$ composite powders was 30 wt.%. The products were composed of granular ZrN as well as columnar and acicular $\beta$-Si$_3$N$_4$. ZrN, $\beta$-Si$_3$N$_4$ and c-ZrO$_2$ were the main components of the products when the amount of quartz was less than 30 wt.%. However, the products consisted of ZrN, $\beta$-Si$_3$N$_4$, Si$_2$N$_2$O, m-ZrO$_2$ and c-ZrO$_2$ when the amount of quartz was 40 wt.% or 50 wt.%. The optimum heating temperature for synthesizing ZrN–Si$_3$N$_4$ composite powders was 1600 °C.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 51032007 and 51272241), the Program for New Century Excellent Talents in University (Grant No. NCET-12-0951) and the New Star Technology Plan of Beijing (Grant No. 2007A080).

Table 2

<table>
<thead>
<tr>
<th>Number</th>
<th>Chemical reactions</th>
<th>$\Delta G^\Theta$ $/J\cdot mol^{-1}$</th>
</tr>
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<tr>
<td>1</td>
<td>Zr(s) + O$_2$(g) = ZrO$_2$(s)</td>
<td>$\Delta G^\Theta_{ZrO_2} = -1092000 + 183.70T$</td>
</tr>
<tr>
<td>2</td>
<td>Zr(s) + 0.5N$_2$(g) = ZrN(s)</td>
<td>$\Delta G^\Theta_{ZrN} = -963600 + 92.00T$</td>
</tr>
<tr>
<td>3</td>
<td>Si(l) + O$_2$(g) = SiO$_2$(s)</td>
<td>$\Delta G^\Theta_{SiO_2} = -946350 + 197.64T$</td>
</tr>
<tr>
<td>4</td>
<td>3Si(l) + 2N$_2$(g) = Si$_3$N$_4$(s)</td>
<td>$\Delta G^\Theta_{Si_3N_4} = -874456 + 405.01T$</td>
</tr>
<tr>
<td>5</td>
<td>2Si(l) + 0.5N$_2$(g) + N$_2$(g) = Si$_2$N$_2$O(s)</td>
<td>$\Delta G^\Theta_{Si_2N_2O} = -951651 + 290.57T$</td>
</tr>
<tr>
<td>6</td>
<td>Si(l) + C(s) = SiC(s)</td>
<td>$\Delta G^\Theta_{SiC} = -114400 + 37.2T$</td>
</tr>
<tr>
<td>7</td>
<td>C(s) + 0.5O$_2$(g) = CO(g)</td>
<td>$\Delta G^\Theta_{CO} = -114400 - 85.77T$</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Reactions equation</th>
<th>$\Delta G^\Theta /J\cdot mol^{-1}$</th>
<th>Logarithm of partial pressure of CO</th>
</tr>
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<tbody>
<tr>
<td>Eq. (4)</td>
<td>$\Delta G^\Theta_1 = 597849 - 362.02T$</td>
<td>$\ln p_{CO} = -2902 + 15$</td>
</tr>
<tr>
<td>Eq. (5)</td>
<td>$\Delta G^\Theta_2 = 603150 - 331.98T$</td>
<td>$\ln p_{CO} = -2862 + 20$</td>
</tr>
<tr>
<td>Eq. (6)</td>
<td>$\Delta G^\Theta_3 = 1278194 - 702.53T$</td>
<td>$\ln p_{CO} = -2092 + 14$</td>
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<tr>
<td>Eq. (7)</td>
<td>$\Delta G^\Theta_4 = 999200 - 526.48T$</td>
<td>$\ln p_{CO} = -2054 + 16$</td>
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</table>
References


