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Thermodynamic Analysis and Preparation of Composites in Zr-Si-C-N-O System

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Abstract: In order to obtain the diagrams of stability relations (namely, predominance area phase diagram, PAPD) for carbothermal reduction and nitridation (CRN) of zircon, the thermodynamic calculation and the analysis on the Zr-Si-C-N-O system were carried on by the method of $\Delta_f G_i^{\Theta} = A + BT$, and PAPD of the Zr-Si-C-N-O system was constructed. The CRN of zircon may lead to the formation of different oxide-nitride composites such as ZrO_2-Si_2N_2O, ZrN-Si_2N_2O, and ZrN-Si_3N_4 by controlling reaction conditions of carbon proportion, temperature, and partial pressures of CO and N_2. Zircon powder (45 μm), activated carbon and N_2 (99.999%) were used as the starting materials, the effect of carbon proportion on the mass loss and the product phase composition after CRN of zircon was investigated. Carbon proportion affects the yielded reaction products obviously; and the higher the carbon proportion, the lower the starting temperature for the CRN to occur.

Key words: zircon; carbothermal reduction and nitridation (CRN); thermodynamic analysis; predominance area phase diagram (PAPD); carbon proportion

Carbothermal reduction and nitridation (CRN) is one of common ways to prepare relatively less costly nonoxides or oxide-nonoxide composite powders for high temperature materials. The costs of these composite powders can be further reduced by using natural raw materials. On the other hand, by using CRN method, the obtained composite powders are usually perfectly homogenized. It is possible to obtain a wide variety of nitrides or oxide-nonoxide composite powders with great scientific and technological interest such as ZrN-Si_3N_4[1-3], ZrO_2-Si_2N_2O[4,5] and $Zr(C,N,O)$[6] quaternary phases by CRN of zircon.

However, the reaction complexity may bring many products during the CRN of zircon, for example, ZrN, ZrC, ZrO_2-Si_2N_2O, ZrO_2-SiC, ZrN-Si_2N_2O and ZrN-Si_3N_4,etc.. The products obtained depend not only on the raw materials used but also on the reaction condition, such as reaction temperature, atmosphere and carbon proportion. Therefore, the thermodynamic calculation and the analysis of Zr-Si-C-N-O system can supply the theory basis for the choice of relevant technological parameters.

The correlation of Zr-Si-C-N-O system at different temperatures and under different partial pressures of CO was analyzed by thermodynamic calculation, the predominance area phase diagram (PAPD) of Zr-Si-C-N-O system was constructed, and the effect of carbon proportion on reaction products was researched.

1 Thermodynamic Calculation and Analysis

1.1 Phase relationship at different temperatures and under different CO partial pressures

The CRN of zircon belongs to Zr-Si-C-N-O system. In this system, the important condensation phases are SiO_2, ZrO_2, SiC, ZrC, Si_3N_4, ZrN, Si_2N_2O and carbon. Table 1 lists the standard Gibbs free energy of the formation of some compounds and elements[7].

According to the thermodynamics data in Table1, the standard Gibbs free energy changes $(\Delta_r G^{\Theta})$ for reactions in the Zr-Si-C-N-O system were calculated and the results are shown in Table 2.

Table 1 Standard Gibbs free energy of formation of different compounds

Reaction equations	$\Delta_f G^{\ominus}=A+BT$/J mol^{-1}	Temperature/ ℃
C(s)+0.5O$_2$(g)=CO(g)	−114400−85.77T	500~2000
Si(s)= Si(l)	50540−30.0T	1412
Si(l)+C(s)=SiC(s)	−114400+37.2T	1412~1727
3Si(l)+2N$_2$(g)=Si$_3$N$_4$(s)	−874456+405.01T	1412~1700
Si(l)+O$_2$(g)=SiO$_2$(s)	−946350+197.64T	1412~1723
2Si(l)+N$_2$(g)+0.5O$_2$(g)= Si$_2$N$_2$O(s)	−951651+290.57T	1412~2000
Zr(s)+O$_2$(g)=ZrO$_2$(s)	−1092000+183.7T	25~1850
Zr(s)+0.5N$_2$(g)=ZrN(s)	−363600+92.0T	25~1850
Zr(s)+C(s)=ZrC(s)	−196650+9.2T	25~1850

Table 2 Standard Gibbs free energy changes for the reactions in the Zr-Si-C-N-O system

Reaction equations	$\Delta_f G^{\ominus}=A+BT$/J mol^{-1}	Equation No.
ZrO$_2$(s)+3C(s)=ZrC(s)+2CO(g)	666550−346.04T	1
ZrO$_2$(s)+2C(s)+0.5N$_2$(g)= ZrN(s)+2CO(g)	499600−263.24T	2
ZrC(s)+0.5N$_2$(g)=ZrN(s)+C(s)	−166950+82.8T	3
2SiO$_2$(s)+3C(s)+N$_2$(g)= Si$_2$N$_2$O(s)+3CO(g)	597849−362.02T	4
SiO$_2$(s)+3C(s)=SiC(s)+2CO(g)	603150−331.98T	5
Si$_2$N$_2$O(s)+3C(s)=2SiC(s)+ CO(g)+N$_2$(g)	608451−301.94T	6
2Si$_2$N$_2$O(s)+C(s)+2/3N$_2$(g)= 4/3Si$_3$N$_4$(s)+2CO(g)	508561−212.67T	7
3SiC(s)+2N$_2$(g)=Si$_3$N$_4$(s)+3C(s)	−531256+293.41T	8
ZrSiO$_4$(s)=ZrO$_2$(s)+SiO$_2$(s)	25496−13.08T	9
2ZrSiO$_4$(s)+3C(s)+N$_2$(g)= 2ZrO$_2$(s)+Si$_2$N$_2$O(s)+3CO(g)	648840−388.25T	10

According to $\Delta_r G^{\theta}$ data of the reactions in Table 2, the relationship between $RT\ln(P_{CO}/P^{\theta})$ and temperature of the reactions (namely PAPD) was plotted. When P_{N_2}=0.1 MPa=P^{θ}, PAPD of Zr-Si-C-N-O system with excessive carbon is shown in Fig.1.

Fig.1 shows that when carbon is excessive, there may be many different products as the temperature and the partial pressure of CO change during the CRN of zircon. For example, when the temperature is 1 500 ℃ (1773 K), with CO partial pressure decreasing, the products change as follows: ZrSiO$_4$→
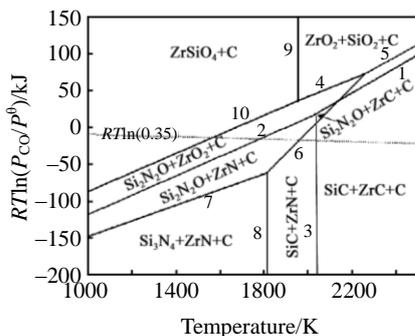

Fig.1 PAPD for the Zr-Si-C-N-O system when P_{N_2}=0.1 MPa

Si$_2$N$_2$O+ZrO$_2$→Si$_2$N$_2$O+ZrN→Si$_3$N$_4$+ZrN. It can be seen from Fig.1 there is no coexistence area for Si$_3$N$_4$ and ZrO$_2$, which means it is infeasible to prepare ZrO$_2$-Si$_3$N$_4$ composite powder by CRN.

For an industrial production, the CRN is often carried out in carbon-embedded condition in air, and CO partial pressure is 0.035 MPa and N$_2$ partial pressure is 0.065 MPa. The thermodynamics calculation shows that when the reaction temperature is lower than 1306 ℃, ZrSiO$_4$ is stabilized phase; when 1306~1518 ℃, Si$_2$N$_2$O+ZrO$_2$; when 1518~1663 ℃, Si$_2$N$_2$O+ZrN; when 1663~1743 ℃, SiC+ZrN; when over 1743 ℃, SiC+ZrC. It can be seen that Si$_3$N$_4$ is unstabilized phase when the CRN of zircon is carried out in carbon-embedded condition in air.

1.2 Phase relationship at same temperature and under different partial pressures

When an excessive carbon coexists, the stability relation-ship of phases in the Zr-Si-C-N-O system has relation not only to the temperature, but also to the partial pressures of CO and N$_2$. Therefore, at a given temperature, the stability relationship of phases in the Zr-Si-C-N-O system should be a function of CO and N$_2$ partial pressure.

According to the data in Table 2, the relationship of $\ln(P_{CO}/P^{\theta})$-$\ln(P_{N_2}/P^{\theta})$ for reactions in Zr-Si-C-N-O system can be calculated. PAPD of the Zr-Si-C-N-O system under various CO and N$_2$ partial pressure at given temperatures is plotted, as shown in Fig.2.

According to Fig.2, when the temperature is given, the products of the CRN of zircon vary with the partial pressures of N$_2$ and CO. For example, at 1723 K（1450 ℃） and when the partial pressure of N$_2$ is equal to 101 325 Pa, with CO par-tial pressure decreasing the products of the CRN of zircon change as follows: ZrSiO$_4$→Si$_2$N$_2$O+ZrO$_2$→Si$_2$N$_2$O+ZrN→Si$_3$N$_4$+ZrN; at 1 823 K (1550 ℃), the products change as fol-lows: with CO partial pressure decreasing, ZrSiO$_4$→Si$_2$N$_2$O+ZrO$_2$→Si$_2$N$_2$O+ZrN→SiC+ZrN. At 1773 K （1500 ℃）, when the partial pressure of N$_2$ is equal to 101 325 Pa, to obtain Si$_3$N$_4$+ZrN composite powder, CO partial pressure must be lower than 1172 Pa, otherwise, the products will be Si$_2$N$_2$O+ZrN or Si$_2$N$_2$O+ZrO$_2$.

2 Experiment

2.1 Specimen preparation

Commercially available zircon powder (45 μm) was used as the starting material. The chemical analysis of the powder, given by the manufacturer, is as follows: 66.59% ZrO$_2$, 32.52% SiO$_2$, 0.19% TiO$_2$ and 0.08% Fe$_2$O$_3$. Commercial activated carbon(analytical reagent, AR) was used as carbon source and N$_2$ with 99.999% of purity (O$_2$≤3.0×10^{-6}，H$_2$O≤ 5.0×10^{-6}) as nitrogen source.

The thermodynamics analysis results show that different carbon proportions result in the formation of different reaction products during the CRN of zircon. According to Fig.1, the
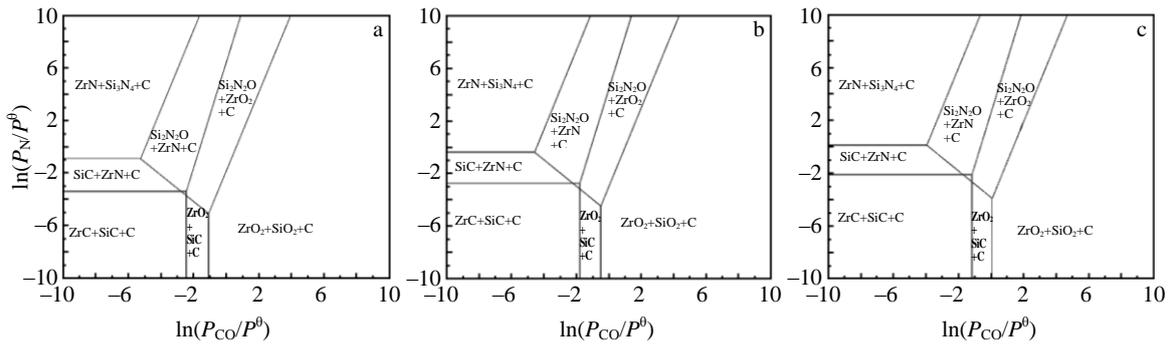
Fig.2 PAPD for the Zr-Si-C-N-O system at given temperatures: (a) 1723 K, (b) 1773 K, and (c) 1823 K

chemical reactions and their theoretical mass losses for the calculation of carbon proportions are shown in Table 3.

Considering a possible carbon loss in the preparation of specimens the actual carbon proportion should be slightly higher than the theoretical value, the actual carbon proportion was therefore set at 10%, 20%, 22% and 30%, respectively. The specimens were coded by a letter A, for activated carbon, followed by carbon proportion data. In this way, we obtained A10 (carbon proportion 10%), A20 (carbon proportion 20%), A22 (carbon proportion 22%) and A30 (carbon proportion 30%) specimens.

Using water as disperse medium, the starting materials were wet-mixed for 24 h in a ball mill according to the calculated amounts, dried at 110 ℃ for 24 h and then pressed under 50 MPa into the cylinder specimens with 8~10 mm in height and 36 mm in diameter. After dried at 110 ℃ for 24 h, the specimens were put in a graphite crucible; the crucible was placed in an atmosphere-controlled muffle furnace with $MoSi_2$ heating elements, heated to 1450, 1500 ℃ and soaked for 4 h and then cooled to ambient temperature along the furnace. The reactions were performed in nitrogen atmosphere with a gas flow rate of 500 L h^{-1}. In all experiments a N_2 pressure of 0.02 MPa above the atmospheric pressure was used.

2.2 Properties testing

The phase composition after reaction was characterized by XRD with Philips X′ Pert Pro MPD equipment using Cu-Kα radiation and Ni filter at 40 kV and 40 mA. The scanning was made at room temperature between 6° and 76° in 2θ with step

size of 0.02° and a step counting time of 2 s. The crystalline phases were expressed in mass fraction (wt%), and percentages of different phases were calculated by a RIR method.

$$W_x = \frac{I_x}{K_x(I_1/K_1 + I_2/K_2 + \cdots\cdots + I_n/K_n)} \times 100\% \quad (1)$$

where, W_x is the relative content of x phase in the sample, L_x is the absolute intensities of diffraction peaks of x phase and K_x is the RIR value of x phase

The CRN of zircon is followed by the mass loss, the mass change is determined by weighting the specimens before and after heat treatment to calculate the actual mass loss ratio for characterizing the reaction degree of the specimen.

$$W_L = \frac{m_1 - m_2}{m_1} \times 100\% \quad (2)$$

where, W_L is the actual mass loss ratio of specimen, m_1 is the specimen mass before the reaction, and m_2 is the specimen mass after the reaction.

3 Results and Discussion

3.1 Effect of carbon proportion on mass loss ratio and phase containing silica of the specimens

The comparison of the actual mass loss ratio and the theoretical mass loss ratio of all the specimens after reacted at 1500 ℃ is shown in Fig.3. The effects of carbon proportion on the ratio of Si_2N_2O and the decomposed zircon and the contents of $ZrSiO_4$ are shown in Fig.4a and Fig.4b, respectively.

Table 3 Carbon proportion and theoretical mass loss of different reactions (wt%)

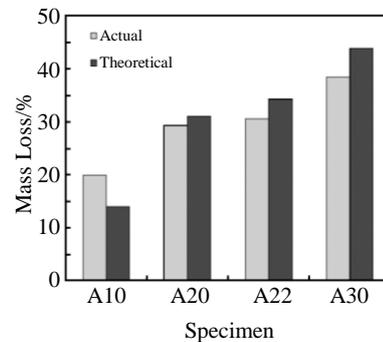| Reaction equations	Carbon proportion	Theoretical mass loss
$2ZrSiO_4+3C+N_2=$ $Si_2N_2O+2ZrO_2+3CO$	8.95	13.9
$2ZrSiO_4+7C+2N_2=$ $Si_2N_2O+2ZrN+7CO$	18.7	31.1
$6ZrSiO_4+24C+7N_2=$ $2Si_3N_4+6ZrN+24CO$	20.8	34.3
$ZrSiO_4+6C=SiC+ZrC+4CO$	28.2	43.9

Fig.3 Effect of carbon proportion on mass loss of CRN of zircon after reacted at 1500 ℃ for 4 h
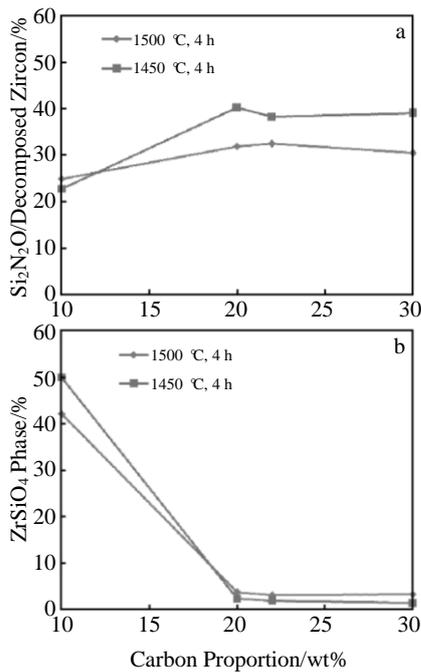
Fig.4   Effect of carbon proportion on Si_2N_2O/decomposed zircon ratio (a) and content of $ZrSiO_4$ (b)

It can be seen from Fig.3a, when carbon proportion is 10%, the actual mass loss is larger than the theoretical value calculated from Fig.3. It may be explained by the following equation:

$$ZrSiO_4+C \rightarrow ZrO_2+SiO(g)+CO(g) \qquad (3)$$

The high mass loss results from SiO volatilization. However, in other specimens with higher carbon proportion, the actual mass loss is smaller than the theoretical mass loss. Moreover, the higher the carbon proportion is, the bigger the difference between the actual mass loss ratio and the theoretical one is. This fact can be explained by the following equations:

$$3SiO(g)+3C+2N_2 \rightarrow Si_3N_4+3CO(g) \qquad (4)$$
$$2SiO(g)+C+N_2 \rightarrow Si_2N_2O+CO(g) \qquad (5)$$

Fig.4a shows that the ratios of Si_2N_2O and the decomposed zircon in the samples increase obviously with carbon proportion increasing from 10% to 20%, which means with the increase of carbon proportion, the volatilization of SiO decreases. Therefore, the carbon proportion can be increased for improving the content of silicon-rich phases such as Si_2N_2O, Si_3N_4 or SiC. However, this results in residual free carbon after reaction, which can hardly be eliminated without degrading the nitride.

3.2   Effect of carbon proportion on phase composition of the specimens

Fig.5 shows the XRD patterns of the samples with different carbon proportions after reacted at 1500 ℃ for 4 h.

The expected products of sample A10 are ZrO_2 and Si_2N_2O according to the thermodynamics analysis, but the actual products of sample A10 include m-ZrO_2, Si_2N_2O, undecomposed $ZrSiO_4$ and intermediate phase $Zr_7N_8O_4$, as shown in Fig.5.
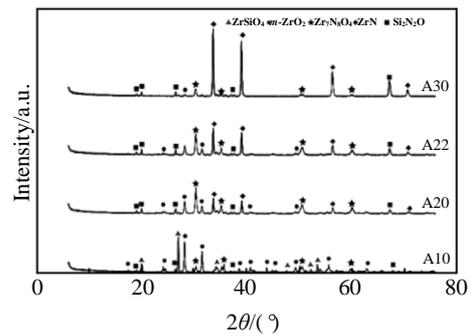

Fig.5   XRD patterns of the samples with different carbon proportions after heat treated at 1500 ℃ for 4 h

During the phase analysis of the samples after heat treated, $Zr_7O_8N_4$ is identified as c-ZrO_2 at first because the $Zr_7N_8O_4$ phase shows the diffraction peaks which are very similar to that of c-ZrO_2, except that some additional very small superlattice reflections cannot be observed in c-ZrO_2[8,9]. It is well known that c-ZrO_2 is hard to exist stably at room temperature without the existence of stabilizer. In this work the stabilizer isn't introduced. How is the existence of c-ZrO_2 explained? Claussen et al.[10] researched the phase composition after the nitridation of ZrO_2 and called this phase as 'nitrogen stabilized cubic zirconia'. While Lerch et al.[11] regarded that this phase is zirconium nitrogen oxide and called it as β-type phase, which it is the general term of $\beta(Zr_7O_8N_4)$, $\beta'(Zr_7O_{11}N_2)$ and $\beta''(Zr_7O_{9.5}N_3)$ in ZrO_2-Zr_3N_4 binary system with general chemical formula of $ZrO_{2-2x}N_{4x/3}$, as shown in Fig.6.

In order to prove that the c-ZrO_2 should be zirconium oxynitride, the specimen A30 was fired at 1500 ℃ for 4 h in Ar atmosphere, and its XRD pattern is shown in Fig.7.

Fig.7 shows that the products of A30 after reacted in Ar atmosphere include m-ZrO_2, ZrC and SiC, while c-ZrO_2 phase is not formed. This fact confirms that c-ZrO_2 in the CRN products of zircon is zirconium oxynitrides. XRD analysis shows that the yielded zirconium oxynitride mainly consists of β phase with chemical formula of $Zr_7O_8N_4$ in this work.
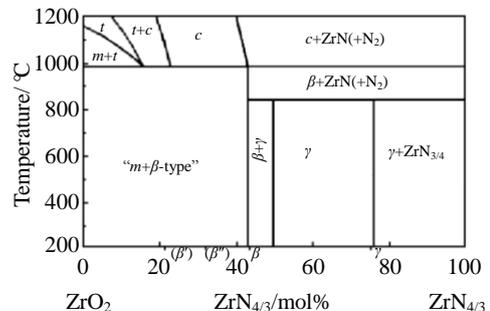
According to thermodynamic analysis, the expected prod-

Fig.6   Observed phases in ZrO_2–Zr_3N_4 system (c: cubic fluorite structure; t: tetragonal distorted fluorite structure; m: monoclinic baddeleyite structure; $\beta/\beta'/\beta''$: β-type phases)[11]
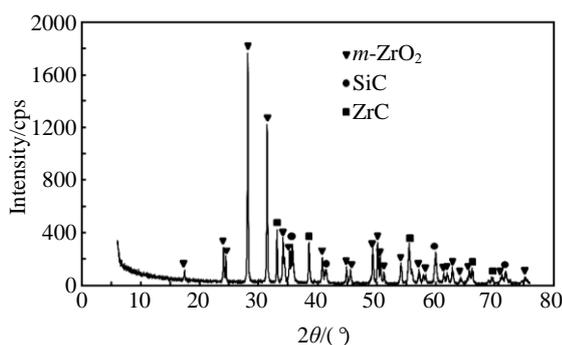
Fig.7 XRD pattern of the sample A30 after reaction in Ar atmosphere at 1500 ℃ for 4 h

ucts of sample A20 are ZrN and Si_2N_2O. Besides these expected phases, the actual product phases also include much m-ZrO_2 and $Zr_7O_8N_4$, and a trace of undecomposed $ZrSiO_4$. XRD semi-quantitative analysis shows that the content of Si_2N_2O is consistent with the expect value, but the content of ZrN is less than the expect value, only about 10 wt%. The main reason can be attributed to the reaction unbalance, which depends on the parameters of dynamic such as temperature and time.

When carbon proportion is larger than 22 wt%, the expected phases of samples are ZrN and Si_3N_4. In fact the products are ZrN, Si_2N_2O, little $Zr_7O_8N_4$ and m-ZrO_2, and a trace of $ZrSiO_4$. The actual product being Si_2N_2O instead of Si_3N_4 mainly is because of the higher practical pressure of CO or low reaction temperature.

In sample A10 the amount of undecomposed zircon after reacted at 1500 ℃ is still very high as shown in Fig.4b and Fig.5. While in other samples, the content of $ZrSiO_4$ is lower than 3wt%, meaning that the zircon has disappeared after reacted at 1450 ℃. This result shows that the increase of carbon proportion can accelerate the decomposition of $ZrSiO_4$. Therefore, the starting temperature of reaction can decrease by

increasing of carbon proportion.

4　Conclusions

1) The stability domains of product phases for CRN of zircon have relation to processing parameters such as reaction temperature, partial pressures of CO and N_2. Different oxide-nitride composite materials such as ZrO_2-Si_2N_2O, ZrN-Si_2N_2O, and ZrN-Si_3N_4 can be prepared by controlling carbon proportion and reaction conditions. $Zr_7O_8N_4$ is an intermediate phase in these reactions.

2) Different carbon proportions result in different reaction products. With the increase of carbon proportion, the starting temperature of CRN of zircon decreases.

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Zr-Si-C-N-O 系复相材料的制备及热力学分析

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摘　要：为了得到锆英石碳热还原氮化反应时产物相的稳定存在区域，用 $\Delta_f G_i^\ominus = A + BT$ 法对Zr-Si-C-N-O系进行了热力学计算和分析，绘制了Zr-Si-C-N-O系优势区相图。结果表明：通过控制配碳量、反应温度、炉内的CO分压和N_2分压，可以获得组成分别为ZrO_2-Si_2N_2O、ZrN-Si_2N_2O或ZrN-Si_3N_4等的复相材料。根据热力学分析结果，以锆英石、活性炭为原料，N_2（99.999%）为氮源，研究了配碳量（10%，20%，22%，30%，质量分数）对锆英石碳热还原氮化反应失重率及产物相组成的影响。结果表明：配碳量不仅显著影响锆英石碳热还原氮化反应产物的物相组成，而且配碳量的增加还会降低锆英石碳热还原氮化反应的开始温度。

关键词：锆英石；碳热还原氮化；热力学分析；优势区相图；配碳量

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