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ORIGINAL RESEARCH

Novel approaches to produce Al$_2$O$_3$–TiC/TiCN–Fe composite powders directly from ilmenite

Aitao Tang[a,b,*], Shengming Liu[a,b], Fusheng Pan[a,c]

[a]College of Materials Science and Engineering, Chongqing University, Chongqing 400045, China
[b]National Engineering Research Center for Magnesium Alloys, Chongqing 400044, China
[C]Chongqing Academy of Science & Technology, Chongqing 401123, China

Abstract Al$_2$O$_3$–TiC/TiCN–Fe composite powders were successfully prepared directly from ilmenite at 1300–1400 °C. The effects of Al/C ratio, sintering atmosphere, and reaction temperature and time on the reaction products were investigated. Results showed that the nitrogen atmosphere was beneficial to the reduction of ilmenite and the formation of Al$_2$O$_3$–TiC/TiCN–Fe composite powders. When the reaction temperature was between 600 and 1100 °C, the intermediate products, TiO$_2$, Ti$_3$O$_5$ and Ti$_4$O$_7$ were found, which changed to TiC or TiCN at higher temperature. Al/C ratio was found to affect the reaction process and synthesis products. When Al addition was 0.5 mol, the Al$_2$O$_3$ phase did not appear. The content of carbon in TiCN rose when the reaction temperature was increased.

1. Introduction

Alumina ceramics (Al$_2$O$_3$) have been used in the industry due to their low density, high hardness and good chemical inertness [1]. However, alumina ceramics have poor fracture toughness and thermal shock resistance, and wider application is limited. The incorporation of some second particulate phases into the ceramic matrix has been known to improve the mechanical properties of ceramics, such as the resistance to crack initiation and propagation. Among common reinforcing phases, TiC or TiCN with the same crystal structure as NaCl is preferred for its high hardness, low density, high melting point, high elastic modulus, excellent wear and corrosion resistance, appropriate electrical conductivity, high thermal shock resistance, and good wettability and stability in iron melt [2–6]. As a result, TiC or TiCN has been extensively utilized in Al$_2$O$_3$–TiC/TiCN composites and Fe-based compostes [7–9], and application of TiC or TiCN in surface coatings are also being investigated [10,11].

However, the TiC or TiCN powders prepared by traditional methods are very expensive, and many researchers tried to develop

*Corresponding author at: College of Materials Science and Engineering, Chongqing University, Chongqing 400045, China. Tel: +86 23 65106121.

E-mail address: tat@cqu.edu.cn (A. Tang).

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low cost preparing processes for TiC or TiCN powders. Ilmenite ($FeTiO_3$) is not only cheap but also very rich in China. The preparation of TiC or TiCN powders directly from ilmenite is very potential [12,13]. Besides, the surface contamination of the reinforcements is not avoidable when TiC or TiCN powders are added to Al_2O_3. The in-situ fabrication technique directly from ilmenite, aluminum and carbon not only overcomes the aforementioned disadvantages but also produces thermodynamically stable and impurity-free interfaces, similar to MC carbides in tool steels [14]. Therefore, the in-situ composites can result in better mechanical properties than traditionally processed composites [15].

Reaction synthesis of $FeTiO_3$–Al–C has attracted increasing interest. However, previous studies focused mainly on the formation of Fe–Al/Al–Ti intermetallic compounds using $FeTiO_3$–Al mixture [15–20], or TiO_2 was used to replace $FeTiO_3$, which is not cheap compared to $FeTiO_3$ [1,18,19,21–28]. Very few works on the direct synthesis of Al_2O_3–TiC/TiCN powders from ilmenite has been carried out.

In the present work, very cheap ilmenite ($FeTiO_3$) is used as one of starting materials. The reaction synthesis of Al_2O_3–TiC/TiCN–Fe composite powders from the mixture of ilmenite, Al and C was investigated, and the intermediate products during the reaction processes of the $FeTiO_3$–Al–C system at different reaction temperature were analyzed.

2.   Experimental

Ilmenite ($FeTiO_3$, Panzhihua mineral from China), Al, and graphite powders were used as raw materials in the experiments. Al and graphite powders were used as reducing agents. Mixtures were prepared in accordance with Eq. (1), which is the thermodynamically predicted reaction:

$$FeTiO_3 + xAl + (4-3x/2)C \rightarrow TiC + (x/2)Al_2O_3 + Fe + (3-3x/2)CO$$
(1)

x value changes from 0.5 to 1.5 mol for investigating the effects of Al addition on the reaction processes. The powder blend of ilmenite, Al, and graphite was ball milled for 4 h in a vertical planetary ball mill (QM-3SP4, China). The mill was operated at a speed of 300 rpm using different diameters of steel balls (6 and 10 mm). The mass ratio of ball-to-powder was maintained at 12:1. Ball milling was performed under an air atmosphere at room temperature.

Approximately 20 g of the mixture was placed into a graphite crucible in a sintering furnace after milling. The furnace was evacuated to vacuum and then filled with flowing argon or nitrogen. Atmosphere flow rate was at 1 L/min. In order to understand the characteristics of the synthesis process, the samples were sintered for 30 min at different temperatures.

The starting materials, milled powders, and reaction products were characterized by XRD (D/MAX-1200, China) using Cu $K\alpha$ radiation within the range $10°$ to $90°$. Peak positions were acquired from the International Center for Diffraction Data database. Raw XRD data were refined and analyzed through the MDI Jade 6.0 program (Materials Data Incorporated, Livermore, California, USA). NIST silicon powder (SRM640) was used as an external standard for correction because of instrumental broadening. Experimental errors were reduced as much as possible by fitting the curve. The microstructures of the sintered specimens were investigated using a scanning electron microscope (SEM) (TESCAN VEGAIILMU) equipped with

an energy-dispersive X-ray spectroscopy system for elemental analysis (Oxford INCA).

3.   Results

The XRD patterns of as-milled powders with different Al additions are shown in Fig. 1. The phases shown by the XRD patterns included the $FeTiO_3$, Al, and C phases, and no any new phases were found. This suggests that no significant reactions occur among the mixture of $FeTiO_3$, Al, and C during milling. The intensity of the Al peaks significantly increased with increasing Al content, whereas the intensity of the C peaks gradually decreased.

3.1.   Reaction in argon atmosphere

To understand the reaction process of the $FeTiO_3$–xAl–$(4-3x/2)C$ system in argon atmosphere, the $FeTiO_3$–1Al–2.5C system consisting of 1 mol $FeTiO_3$, 1 mol Al, and 2.5 mol C was investigated. Fig. 2 shows the XRD patterns of the $FeTiO_3$–1Al–2.5C mixture powders sintered at different temperatures for 0.5 h in argon atmosphere.

The results showed that no any new phases appeared as the sample heated at 600 °C, which suggests that no action occurred at 600 °C. When the sample was heated up to 700 °C, TiO_2, Ti_4O_7 and Ti_3O_5 were found, whereas ilmenite and Al disappeared, which indicated that ilmenite and Al reactions occurred during heating at 700 °C. In same cases, the compounds of iron and carbon, such as Fe_3C, was also found, and disappeared at higher temperature. TiO_2 is the initial reduction product from ilmenite. Fig. 2 shows that the intensity of TiO_2 phase decreased gradually as temperature increased, and TiO_2 disappeared at 900 °C, whereas the intensity of the Ti_3O_5 and Ti_4O_7 strengthened. The results in Fig. 2 suggest that the Ti_3O_5 and Ti_4O_7 phases form by the reaction of TiO_2 and Al. It was found that Al_2O_3 and Fe phase formed when oxides of titanium occurred. The results evidently showed that the following reactions occurred at 700 °C:

$$3FeTiO_3 + 2Al \rightarrow 3TiO_2 + Al_2O_3 + 3Fe$$
(2)

$$9TiO_2 + 2Al \rightarrow 3Ti_3O_5 + Al_2O_3$$
(3)
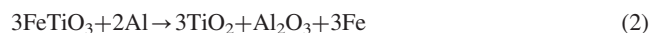
It was found that TiC peaks appeared at 1000 °C. When temperature increased from 1100 to 1300 °C, the intensity of Ti_3O_5 and carbon
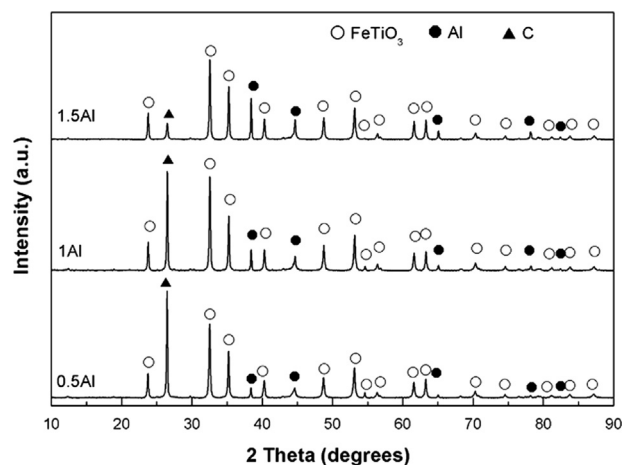

Fig. 1   XRD patterns of $FeTiO_3$–Al–C milled powders with the starting compositions given in Eq. (1) ($x = 0.5, 1, 1.5$ mol).
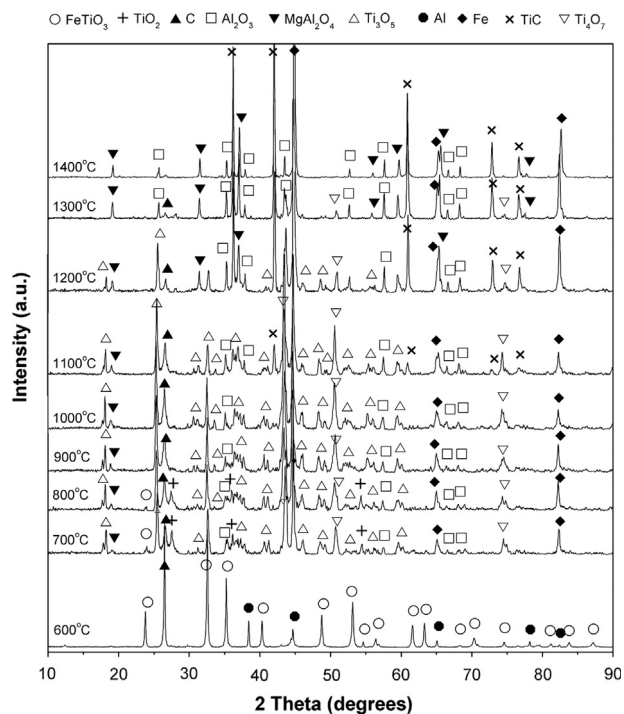
Fig. 2 XRD patterns of FeTiO$_3$–1Al–2.5C milled powders and samples annealed for 0.5 h at different temperatures in argon atmosphere.

peak gradually weakened. When carbon began to participate in the reaction, and the TiC phase occurred. The intensity of TiC peaks increased with increasing temperature, as shown in Fig. 3a. This finding shows that the formation of TiC occurs from the reaction between Ti$_3$O$_5$ or Ti$_7$O$_4$ and C at about 1100 °C:

$$Ti_3O_5 + 8C \rightarrow 3TiC + 5CO \qquad (4)$$

$$Ti_4O_7 + 11C \rightarrow 4TiC + 7CO \qquad (5)$$

Another compound, MgAl$_2$O$_4$, was also found in the reaction products because there are some impurity of MgO in ilmenite, which can be also used as a reinforcement in the composites. When the temperature increased to 1300 °C, the Ti$_3$O$_5$ and Ti$_7$O$_4$ phases disappeared. The little change of the position of TiC peak in Fig. 3 was found, which was identified that there were some oxygen atoms in the early TiC carbide. The final products were composed of Al$_2$O$_3$, MgAl$_2$O$_4$, TiC, and α-Fe.

The effects of aluminum content on the reaction products are shown in Fig. 4. The results clearly showed that the reaction products differed with changes in Al content. When Al content was 0.5 mol, the major titanium-containing phase was TiO$_2$, whereas the minor titanium-containing compounds were FeTiO$_3$ and Ti$_3$O$_5$. When Al content was increased to 1 mol, the predominant titanium-containing compound was Ti$_3$O$_5$, and the remaining titanium-containing phases were FeTiO$_3$ and TiO$_2$. Finally, a large amount of TiC with small amounts of Ti$_3$O$_5$ and TiO$_2$ residues was formed when Al content is further increased to 1.5 mol. These results indicate the acceleration of the reaction process with increasing Al content because of the powerful reduction capacity of Al. In addition, the cementite (Fe$_3$C) was found at 800 °C when Al content was increased to 1.5 mol, which disappeared at temperature of higher than 1100 °C.

Fig. 5 shows the XRD patterns of the as-milled powders sintered for 2 h at 1400 °C in argon atmosphere. As expected,
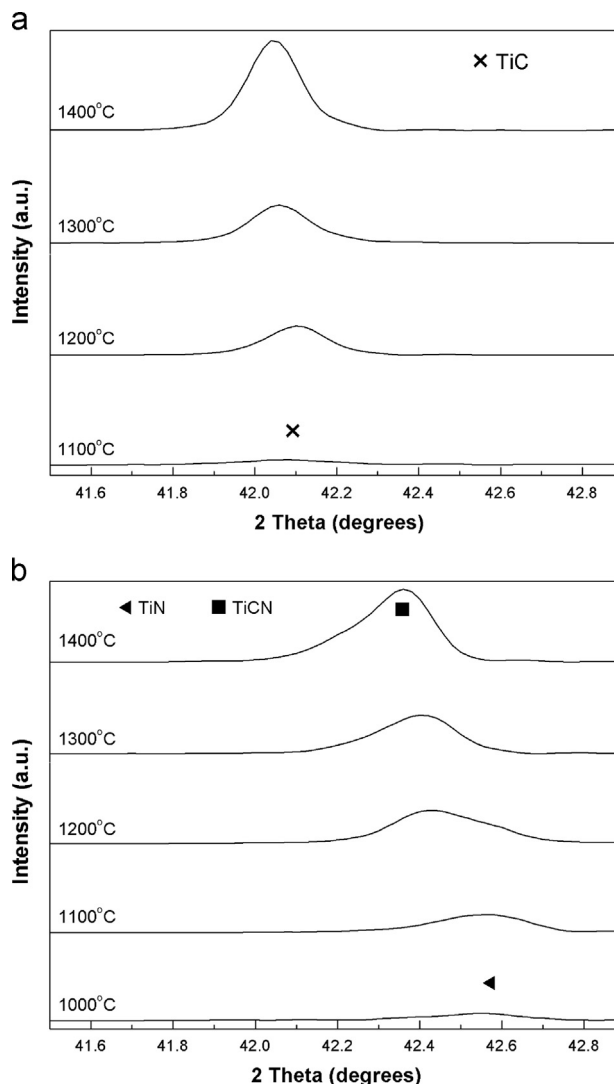

Fig. 3 XRD patterns of the samples sintered at different temperatures: (a) TiC phase in argon atmosphere and (b) TiCN phase in nitrogen atmosphere.

Al$_2$O$_3$, TiC and Fe were identified when Al addition is 1 and 1.5 mol. No any Al$_2$O$_3$ phase appeared when Al content was 0.5 mol, but MgAl$_2$O$_4$ was formed instead. The diffraction position of the TiC phase was almost the same for all the samples, which means that the lattice parameters of the TiC phase keep almost unchanged (Table 1).

Backscattered electron images of specimens, prepared from the FeTiO$_3$–xAl–(4−3x/2)C (x=0.5, 1, 1.5 mol) system sintered for 2 h at 1400 °C in argon atmosphere, are shown in Fig. 6. Al$_2$O$_3$/MgAl$_2$O$_4$ is dark, TiC is gray, and the Fe phase is brightly colored in the images. The average size of composite powders, which is less than 3 μm, is similar to that of commercial powders.

3.2.   Reaction in nitrogen atmosphere

Figs. 7 and 8 show part of the XRD patterns of the FeTiO$_3$–1Al–2.5C powders sintered at varying temperatures for 0.5–2 h in nitrogen atmosphere. No significant differences were observed
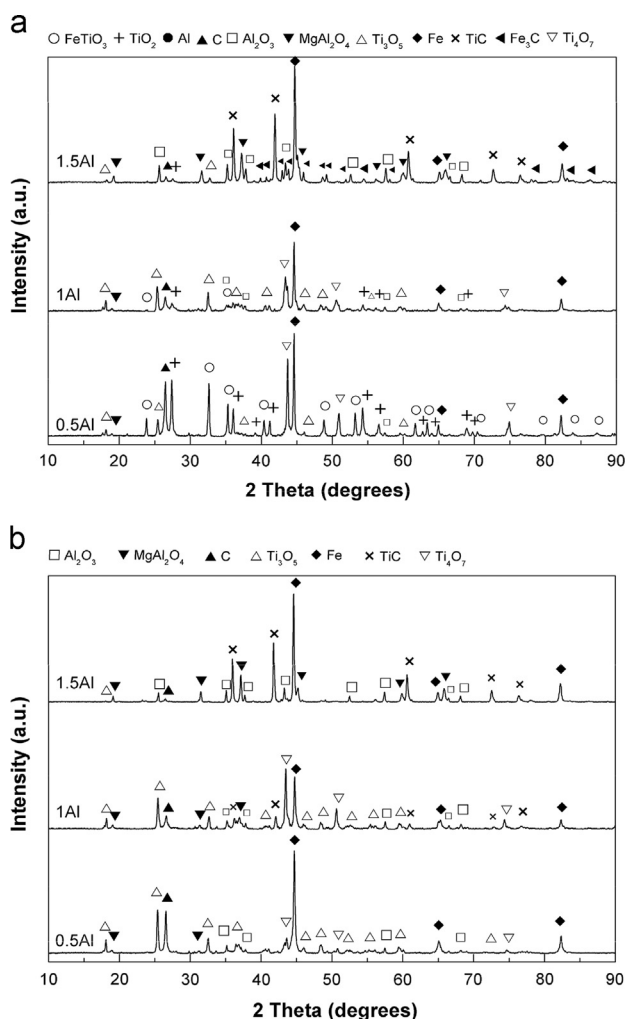
a

○ FeTiO₃ + TiO₂ ● Al ▲ C □ Al₂O₃ ▼ MgAl₂O₄ △ Ti₃O₅ ◆ Fe × TiC ◀ Fe₃C ▽ Ti₄O₇

b

□ Al₂O₃ ▼ MgAl₂O₄ ▲ C △ Ti₃O₅ ◆ Fe × TiC ▽ Ti₄O₇

Fig. 4 XRD patterns of FeTiO₃–xAl–(4−3x/2)C milled powders (x=0.5, 1, 1.5 mol) annealed for 0.5 h in argon atmosphere (a) at 800 °C and (b) at 1100 °C.

▼ MgAl₂O₄ □ Al₂O₃ × TiC ◆ Fe

Fig. 5 XRD patterns of FeTiO₃–xAl–(4−3x/2)C milled powders annealed for 2 h at 1400 °C in argon atmosphere (x=0.5, 1, 1.5 mol).

Table 1 Lattice parameters of TiC for FeTiO₃–xAl–(4−3x/2) C system at 1400 °C in argon atmosphere (x=0.5, 1, 1.5 mol).

Al content (mol)	0.5Al	1Al	1.5Al
Lattice parameter (nm)	0.43152	0.43133	0.43130

when the temperature changed from 600 to 900 °C compared with the case in argon atmosphere. When the temperature increased to 1000 °C, TiN peaks appeared.

It was found that the peaks of Ti₃O₅ disappeared at 1300 °C in argon atmosphere but disappeared at 1200 °C in nitrogen atmosphere. The result suggested that the reduction process of the reactions was affected by the presence of nitrogen, which resulted in an accelerated reaction rate. With the increase of temperature, the intensity of the TiN peaks increased and the peaks of TiN shifted to the left with a small angle (Table 2), which suggested that carbon atoms entered to TiN and TiCN occurred. The higher the temperature was, the more carbon atoms there were in TiCN.

The amount of Al addition was also found to have obvious influence on the reaction process. Fig. 8 shows the XRD patterns of as-milled powders sintered for 2 h at 1400 °C in nitrogen atmosphere. When Al addition was 0.5 mol, no any Al₂O₃ was found, which was the same as the result in argon atmosphere. The final reaction products were Al₂O₃, MgAl₂O₄, TiCN, and α-Fe when Al addition was 1 or 1.5 mol. The backscattered electron image of the powders is shown in Fig. 9. The diffraction positions of the TiCN phase were found to be almost the same, and the
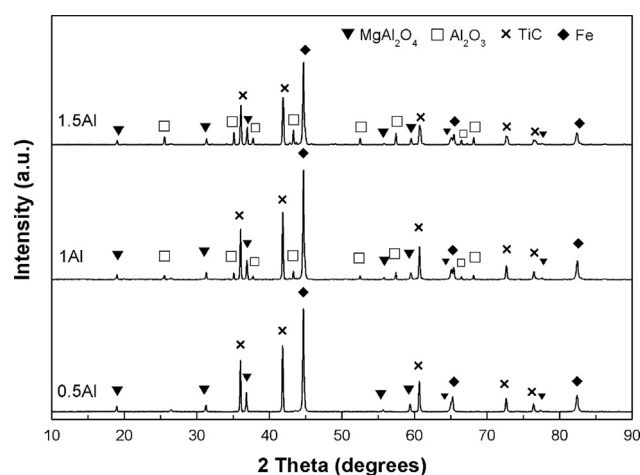
lattice parameters of the TiCN phase are shown in Table 3. According to the relationship between $TiC_{1-x}N_x$ crystal lattice constant and x value, the TiCN composition is $TiC_{0.3}N_{0.7}$.

4. Discussions

The reduction of ilmenite by carbon and aluminum in argon atmosphere proceeds in three main stages: reduction of ilmenite to iron and rutile, reduction of rutile to phases of the general form Ti_xO_y, and reduction of Ti_xO_y to the cubic phase (TiC). At each step, Al₂O₃ can occur from titanium oxides or directly from ilmenite, and the amount of Al₂O₃ increases with the raise of temperature. The cubic phase is formed at the beginning of the third reaction step. The reaction sequence is ilmenite→TiO₂→Ti_xO_y (Ti₃O₅ and Ti₇O₄)→TiC. Before the formation of TiC, TiCO firstly occurs and finally changes to TiC with the further increase of reaction temperature. In nitrogen atmosphere, TiN firstly occurs and finally changes to TiCN, which is agreed with the previous investigators [29–31]. The present results show that the transition from TiN to TiCN is accompanied by a gradual decrease in the amount of both carbon and titanium oxide, which suggests that carbon involvement in the reaction begins at a high temperature. With the increase of temperature and time, the C content in TiCN increases. As the result, the peak position of XRD patterns for TiCN moves from right to left, which is caused by the increase of lattice parameters of TiCN.

Thermodynamic calculation results (Fig. 10) show that the direct synthesis of the Al₂O₃–TiC/TiCN–Fe composite powders from ilmenite is practical above 1300 °C in argon atmosphere and above 1200 °C in nitrogen atmosphere. The nitrogen atmosphere
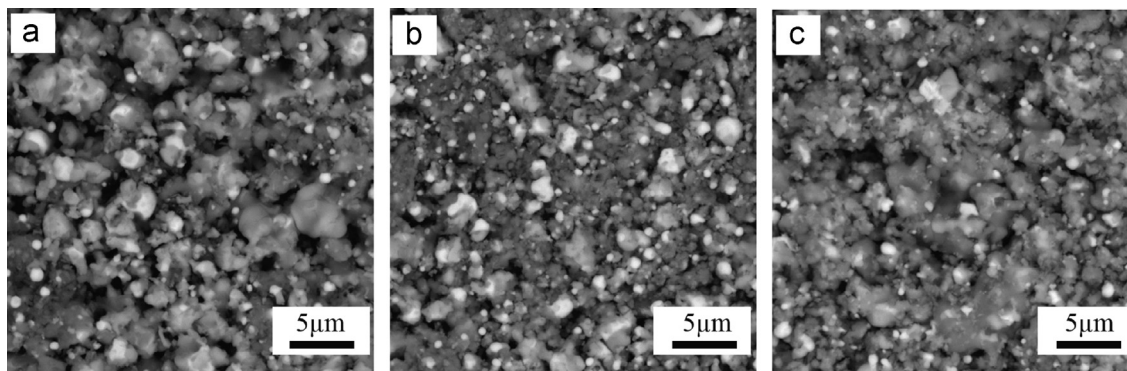
Fig. 6 SEM backscattered electron micrographs of the reaction products at $FeTiO_3$–xAl–$(4-3x/2)$C sintered specimens in argon atmosphere ($x=0.5$, 1, 1.5 mol).
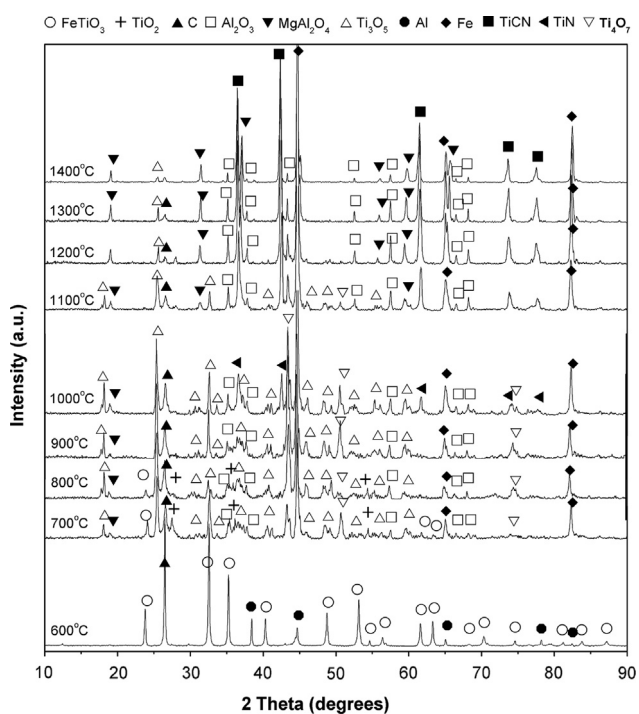

Fig. 7 XRD patterns of $FeTiO_3$–1Al–2.5C milled powders and samples annealed for 0.5 h at varying temperatures in nitrogen atmosphere.

Fig. 8 XRD patterns of $FeTiO_3$–xAl–$(4-3x/2)$C milled powders ($x=0.5$, 1, 1.5 mol) annealed for 2 h at 1400 °C in nitrogen atmosphere.

Table 2 Lattice parameters of TiCN for $FeTiO_3$–1Al–2.5C system at varying temperatures in nitrogen atmosphere.

Temperature (°C)	1000	1100	1200	1300	1400
Lattice parameter (nm)	0.424607	0.424687	0.425490	0.425879	0.426507

is beneficial to the reduction of ilmenite and the formation of composite powders, and aluminum can accelerate the reduction reaction. The calculated results are agreed with the experimental results.

5. Conclusions

(1) The Al₂O₃–TiC/TiCN–Fe composite powders from ilmenite were successfully prepared above 1300 °C in argon atmosphere and above 1200 °C in nitrogen atmosphere. The nitrogen atmosphere was found to be beneficial to the reduction of ilmenite and the formation of composite powders.

(2) When the reaction temperature was between 600 and 1100 °C, the intermediate products, TiO_2, Ti_3O_5 and Ti_7O_4
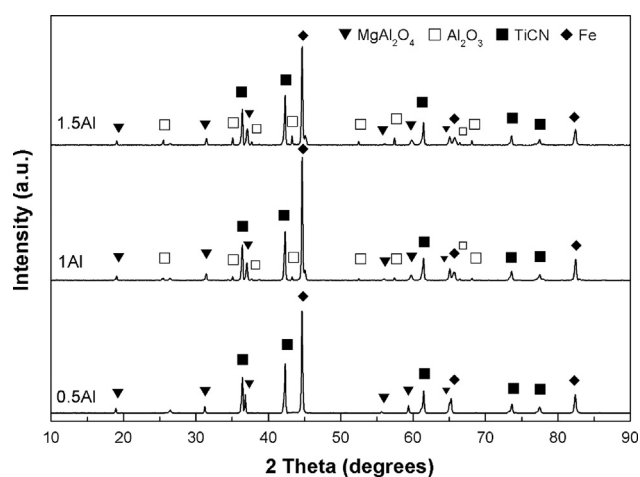
were found, which changed to TiC or TiCN at higher temperature.

(3) Al/C ratio affected the reaction process and synthesis products, and the reaction process was accelerated by Al addition. When Al addition was 0.5 mol, the Al_2O_3 phase did not appear. When Al addition was 1 or 1.5 mol, a lot of Al_2O_3 occurred.

(4) The content of carbon in TiCN increased when the reaction temperature was increased. In the Al_2O_3–TiC/TiCN–Fe composite powders prepared at 1400 °C, the TiCN composition was found to be $TiC_{0.3}N_{0.7}$.
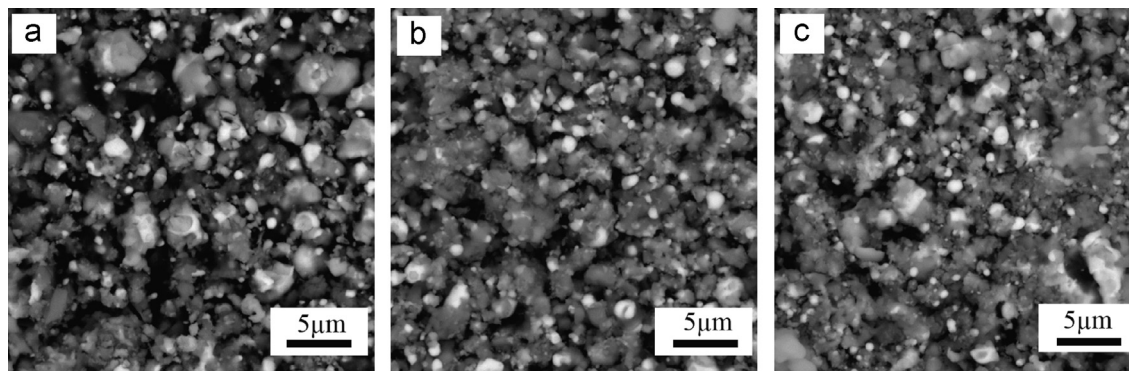
Fig. 9 SEM backscattered electron micrographs of FeTiO$_3$–xAl–(4−3x/2)C sintered specimens in nitrogen atmosphere (x=0.5, 1, 1.5 mol).

Table 3 Lattice parameters of TiCN for FeTiO$_3$–xAl–(4−3x/2)C system at 1400 °C in nitrogen atmosphere (x=0.5, 1, 1.5 mol).

Al content	0.5Al	1Al	1.5Al
Lattice parameter (nm)	0.426381	0.426507	0.426506
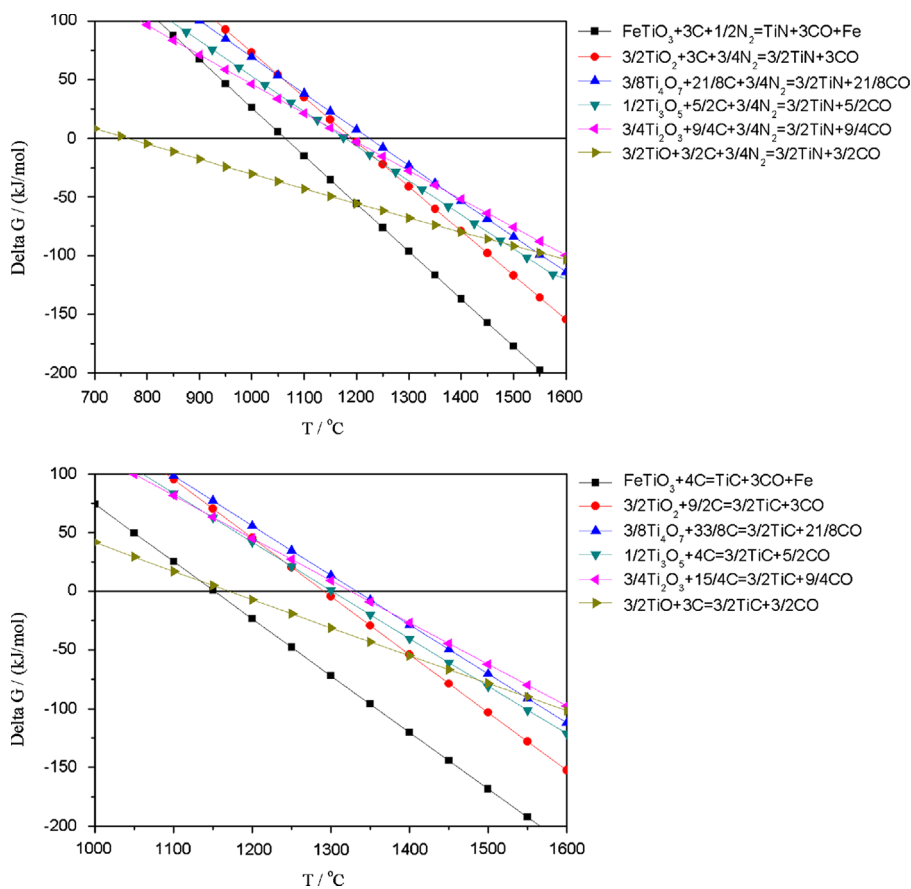
Fig. 10 Thermodynamic calculation results for the reduction of ilmenite.

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