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Synthesis of TiN from FeTiO₃ by microwave-assisted carbothermic reduction–nitridation



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ABSTRACT

Titanium nitride (TiN) was synthesized from ilmenite (FeTiO₃) through the microwave-assisted carbothermic reduction-nitridation followed by acid leaching treatment. The predominance area diagrams of Ti-Fe-N-C-O system at different temperatures were established by Outokumpu HSC Chemistry to analyze the stability of the species concerned. It is demonstrated that titanium and iron oxides can be transformed into TiN-Fe composite by controlling suitable CO and N₂ partial pressures at high temperatures. The TiN-Fe composite can be prepared from FeTiO₃ with microwave heating at 1000 °C for 40 min. TiN was obtained with the removal of iron from TiN-Fe composite by acid leaching at room temperature. The reaction mechanism for the carbothermic reduction-nitridation process was proposed according to experimental results.

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1. Introduction

TiN has been recently attracted increasing interest as a coating material on cutting tools, aircrafts, jigs and fixtures due to its excellent characters such as high hardness, high melting temperature, and good thermal and electrical conductivity [1–4]. The existence of hard TiN particles among the materials increases the wear resistance, shear modulus, and creep property.

These applications are calling for the synthesis of TiN powders with homogeneous chemical composition and small grain size. A number of physical and chemical methods have been reported in literatures for synthesizing nitride. TiN can be produced by direct nitridation of metallic Ti in N₂ atmosphere [5–7], carbothermal reduction of TiO₂ in N₂ atmosphere [8,9] or mechanic alloying and subsequent heat treatment [10,11]. In the last few years, nanometer TiN powder could be synthesized by carbothermal reduction nitridation [12], self-propagating high temperature synthesis [3], low temperature mechanochemical formation [13], pyrolysis of poly(titanylcar-bodiimide) [14], and microwave plasma chemical vapor deposition [15]. Although these methods are considered successful from a commercial point of view, they require expensive raw materials, high temperatures, long reaction time and/or expensive equipment. Another method that has attracted considerable attention is the carbothermic reduction of FeTiO₃ in N₂ atmosphere [14,16-18]. FeTiO₃ is the most important titanium ore which is a naturally occurring and economically mineral with a known world total resource of $\sim 2 \times 10^{12}$ kg [19]. From the viewpoint of thermodynamics, FeTiO₃ can be easily reduced to TiN in N₂ atmosphere by carbon powder compared with TiO₂ raw material. Therefore, it is likely to be more economical for the production of TiN powder with superior quality. However, with traditional heating, a long time up to 21 h and high reaction temperature caused by slow diffusion rates in solids is required to obtain TiN [20-22]. It is necessary to find other more promising and effective heating ways of promoting the reduction process. In recent years there has been a growing interest of microwave heating in the field of material synthesis due to rapid heating, selective material coupling, and enhanced reaction kinetics [23-26]. It has been found that FeTiO₃ and carbon powder have strong ability to absorb microwave energy and can be preferentially and rapidly heated to elevated temperatures [27]. Therefore, the applications of microwave irradiation to the carbothermic reduction-nitridation of FeTiO₃ would be advantageous in shorting reaction time, reducing operation temperature and accelerating reactions.

In this paper, the microwave heating has been used to the carbothermic reduction–nitridation of $FeTiO_3$ with the aim of obtaining TiN–Fe composite with lower operating temperature in N₂ atmosphere. The products prepared were purified by acid leaching process to remove metallic Fe. Its phase transition procedure and influence factors including reaction temperature and reaction time were investigated.

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2. Thermodynamics analysis

The synthesis of TiN from FeTiO₃ includes the preparation of TiN-Fe composite from FeTiO₃ by carbothermic reduction-nitridation and the removal of Fe form the prepared TiN-Fe composite by acid leaching. The carbothermic reduction-nitridation process for synthesizing TiN-Fe composite from FeTiO₃ is a very complex process which involves a series of intermediate reactions. The possible reactions in the process and the corresponding changes in Gibbs free energy are shown in Table 1. The proceeding sequence of the reduction reactions depends on the CO partial pressure, while the formation of TiN depends on both N₂ and CO partial pressures. In order to describe the effect of N₂ and CO partial pressures on the formation of TiN-Fe composite, the predominance area diagrams for the system Ti-Fe-N-C-O at 800 °C, 900 °C and 1000 °C are depicted by Outokumpu HSC Chemistry as shown in Fig. 1, where P_{CO} and P_{N2} are the equilibrium partial pressures of CO and N₂ in gas phase, and P° is standard atmospheric pressure.

Fig. 1 demonstrates that the TiN–Fe composite can be prepared from the oxides by controlling CO and N₂ partial pressures at elevated temperatures, as shown in the shaded areas in the figures. By comparing the shaded areas in Fig. 1, it can be seen that curve abdefg shifts upward gradually as the temperature rises. This implies that the rising of temperature is favorable for the formation of TiN-Fe composite. In addition, the TiN formed is in equilibrium with carbon and oxygen via reaction $C + 1/2O_2 = CO [28]$, hence the residual oxygen and carbon as interstitial atoms may exist in the TiN lattice, which will result in the formation of N, C and O containing phases, such as TiC, TiN_xC_{1-x} ($0 \le x \le 1$), TiC_yO_{1-y} ($0 \le y \le 1$) and TiN_xC_yO_{1-x-y} (x + y = 1; $x, y \ge 0$). Due to lack of the thermodynamic data for TiN_xC_{1-x}, TiC_yO_{1-y} and TiN_xC_yO_{1-x-y}, their possible predominance areas are speculated in accordance with literatures [28,29] and the principles of phase equilibrium, as shown in Fig. 1. Lines ck, ij, bi and hi are the phase boundary between Ti_3O_5 and TiC_yO_{1-y} , TiN_xC_{1-x} and TiN, $TiN_xC_yO_{1-x-y}$ and TiN_xC_{1-x} , $TiN_xC_yO_{1-x-y}$ and TiN, respectively. The values of x, y, and z are determined by composition of N, C, and O. The locations of these lines in the diagram depend on the reaction equilibrium constant K and the values of x, y, and z. Fig. 1 also shows that the reduction of iron oxides is dependent on CO partial pressure and independent off N₂ partial pressure, while the formation of TiN from TiO₂ is determined by CO and N₂ partial pressures at the same time. For example, TiO₂ is firstly reduced to sub-oxides and then reacted with carbon and nitrogen to form $TiN_xC_yO_{1-x-y}$, which is further nitridized to TiN at 1000 °C when $lg(P_{N2}/P^{\circ})$ is lower than 2.88. According to Fig. 1, the phase transition sequence of TiO_2 as a function of N₂ partial pressure can be obtained, as shown in Table 2. It is observed that the intermediate steps from TiO₂ to TiN are increased with decreasing in N₂ partial pressure.

3. Experimental

3.1. Materials

The reduction experiments were conducted with mixtures of FeTiO₃ and carbon powders (99 wt% C). FeTiO₃ powder was synthesized via co-precipitation combined with microwave calcination method and the XRD revealed no evidence of other phases being present. The particle size of FeTiO₃ and carbon powders are both \sim 75 µm. High purity nitrogen (99.99 wt% N₂) which was dried using silica gel and anhydrous potassium hydroxide was used to maintain a reducing atmosphere with a flow rate of 100 mL/min in all experiments.

3.2. Procedures

Before mixing, all the reagents were dried in an oven at 100 °C for 24 h to remove the moisture existed in the raw materials. The samples with a 1:3 M ratio of FeTiO3 to carbon powder were thoroughly mixed and ground with 6 wt% polyvinyl alcohol (PVA). Then the mixtures were pressed with a pressure of 10 MPa in a closed die to obtain a cylindrical pellet (2 mm in height and 13 mm in diameter). The reduction experiments were carried out in a tubular high-temp microwave reactor (2.45 GHz, 3 kW) under nitrogen atmosphere. The pellets were placed in a crucible which was enclosed in a quartz tube (100 cm in length and 8 cm in diameter) and then subjected to microwave irradiation. The sample temperatures with microwave heating were determined by inserting a metallic-sheathed Ni(Cr) thermocouple into the center of sample. The pellets reduced were ground to \sim 75 µm and then leached by HCl solution in a mechanical-agitated vessel for 24 h at room temperature. The agitation speed was held at 500 rpm and the ratio of solid to liquid was maintained constant at 1:4 for all the leaching experiments. The initial concentrations of HCl in leaching solution were 30 wt%. After filtering, the remaining powder was washed several times with distilled water until the pH is about 7, and then dried in a vacuum oven at 100 °C for 12 h.

3.3. Characterization

The products were analyzed by XRD (D/Max-2200 model) with Cu Ka radiation at a scan rate of 10°/min in the range of 2θ = 10–90°. The product X-ray diffraction results were used for determining the lattice parameters of the TiN phase for a given set of processing conditions. SEM (XL 30 ESEM TMP model) was used to estimate the particle size of samples and characterize the morphology of products.

4. Results and discussion

As mentioned above, the carbothermic reduction–nitridation of FeTiO₃ is a complex process. In order to study the effect of microwave heating on the phase changes occurring during the reduction process, the XRD patterns of reaction products for FeTiO₃:C = 1:3 after microwave-assisted carbothermic reduction–nitridation at 800 °C, 900 °C and 1000 °C for different reaction time (10, 20, 40, and 60 min) are shown in Fig. 2. Depending on atmosphere, temperature and reaction time, FeTiO₃ can be reduced and nitridized to different products such as Fe, TiO₂, Ti₂O₃, Ti₄O₇, TiN. From Fig. 2, it is found that FeTiO₃ can be transformed into TiN–Fe composite, which is in a good agreement with the results predicted by thermodynamics.

Table 1

Equations for the changes in Gibbs free energy and $lg(P_{CO}/P^{\circ})-lg(P_{N2}/P^{\circ})$ relationships^a.

Chemical reaction	$\Delta G_T^o(\mathbf{J})$	$lg(P_{CO}/P^{\circ})-lg(P_{N2}/P^{\circ})$ relationships		
		800 °C	900 °C	1000 °C
FeO + C = Fe + CO(g)	111505–154.87T	$lg(P_{CO}/P^{\circ}) = 0.61$	$lg(P_{CO}/P^{\circ}) = 1.24$	$lg(P_{CO}/P^{\circ}) = 1.78$
$9110_2 + C = 11_90_{17} + CO(g)$ $Ti_90_{17} + 5/4C = 9/4Ti_40_7 + 5/4CO(g)$	195676-188.941 284019-251.51T	$lg(P_{N2}/P^{\circ}) = -2.04$ $lg(P_{N2}/P^{\circ}) = -3.35$	$lg(P_{N2}/P^{\circ}) = -1.06$ $lg(P_{N2}/P^{\circ}) = -2.13$	$lg(P_{N2}/P^{\circ}) = -0.27$ $lg(P_{N2}/P^{\circ}) = -1.06$
$3Ti_4O_7 + C = 4Ti_3O_5 + CO(g)$	245699-208.90T	$lg(P_{N2}/P^{\circ}) = -3.77$	$lg(P_{N2}/P^{\circ}) = -2.54$	$lg(P_{N2}/P^{\circ}) = -1.51$
$T_{13}O_5 + 8C = 3T_{1C} + 5CO(g)$ 2TiO ₂ + 4C + N ₂ (g) = 2TiN + 4CO(g)	1101300-836.847 622144-526.34T	$lg(P_{N2}/P^{\circ}) = -4.18$ $lg(P_{N2}/P^{\circ}) = 0.25 \cdot lg(P_{N2}/P^{\circ}) - 2.43$	$lg(P_{N2}/P^{\circ}) = -3.09$ $lg(P_{N2}/P^{\circ}) = 0.25 \cdot lg(P_{N2}/P^{\circ}) - 1.65$	$lg(P_{N2}/P^{\circ}) = -2.18$ $lg(P_{N2}/P^{\circ}) = 0.25 \cdot lg(P_{N2}/P^{\circ}) - 0.99$
$Ti_9O_{17} + 17C + 9/2N_2(g) = 9TiN + 17CO(g)$	2603970-2179.58T	$lg(P_{N2}/P^{\circ}) = 0.27 \cdot lg(P_{N2}/P^{\circ}) - 2.46$	$lg(P_{N2}/P^{\circ}) = 0.27 \cdot lg(P_{N2}/P^{\circ}) - 1.68$	$lg(P_{N2}/P^{\circ}) = 0.27 \cdot lg(P_{N2}/P^{\circ}) - 1.03$
$Ti_4O_7 + 7C + 2N_2(g) = 4TiN + 7CO(g)$ $Ti_2O_5 + 5C + 3/2N_2(g) = 3TiN + 5CO(g)$	1031090-856.92T 711893-590 46T	$lg(P_{N2}/P^{\circ}) = 0.29 \cdot lg(P_{N2}/P^{\circ}) - 2.38$ $lg(P_{N2}/P^{\circ}) = 0.3 \cdot lg(P_{N2}/P^{\circ}) - 2.31$	$lg(P_{N2}/P^{\circ}) = 0.29 \cdot lg(P_{N2}/P^{\circ}) - 1.65$ $lg(P_{N2}/P^{\circ}) = 0.3 \cdot lg(P_{N2}/P^{\circ}) - 1.60$	$lg(P_{N2}/P^{\circ}) = 0.29 \cdot lg(P_{N2}/P^{\circ}) - 1.03$ $lg(P_{N2}/P^{\circ}) = 0.3 \cdot lg(P_{N2}/P^{\circ}) - 1.01$
$2\text{TiN} + 2\text{C} = 2\text{TiC} + \text{N}_2(\text{g})$	259602-164.257	$lg(P_{N2}/P^{\circ}) = -6.21$	$lg(P_{N2}/P^{\circ}) = -4.97$	$lg(P_{N2}/P^{\circ}) = -3.92$

^a For pure solid phases, the all activities of them are assumed to be 1. All thermodynamic data used above comes from Outokumpu HSC Chemistry.



Fig. 1. The predominance area diagram in Ti-Fe-N-C-O system at (a) 800 °C, (b) 900 °C, and (c) 1000 °C. (solid line and dash line: Ti-N-C-O; dash dot line: Fe-N-C-O).

Table 2

The relationship between phase transition sequence and $lg(P_{N2}/P^{\circ})$ at different temperatures^a.

Phase transition sequence	lg (P_{N2}/P°) range at different temperatures		
	800 °C	900 °C	1000 °C
$TiO_2 \rightarrow Ti_9O_{17} \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow TiC_{\gamma}O_{1-\gamma} \rightarrow TiC$	$-8\sim-6.21$	$-8\sim-4.97$	$-8\sim-3.92$
$TiO_2 \rightarrow Ti_9O_{17} \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow TiC_yO_{1-y} \rightarrow TiN_xC_yO_{1-x-y} \rightarrow TiN_xC_{1-x}$	$-6.21 \sim \alpha_1$	$-4.97 \sim \alpha_2$	$-3.92 \sim \alpha_3$
$\text{TiO}_2 \rightarrow \text{Ti}_9\text{O}_{17} \rightarrow \text{Ti}_4\text{O}_7 \rightarrow \text{Ti}_3\text{O}_5 \rightarrow \text{TiC}_y\text{O}_{1-y} \rightarrow \text{TiN}_x\text{C}_y\text{O}_{1-x-y} \rightarrow \text{TiN}_x$	$lpha_1\simeta_1$	$lpha_2\simeta_2$	$\alpha_3 \sim \beta_3$
$TiO_2 \rightarrow Ti_9O_{17} \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow TiN_xC_yO_{1-x-y} \rightarrow TiN$	$eta_1 \sim -4.85$	$eta_2\sim -3.12$	$eta_3 \sim -1.67$
$\text{TiO}_2 \rightarrow \text{Ti}_9\text{O}_{17} \rightarrow \text{Ti}_4\text{O}_7 \rightarrow \text{TiN}_x\text{C}_y\text{O}_{1-x-y} \rightarrow \text{TiN}_x$	$-4.85\sim-3.38$	$-3.12\sim-1.69$	$-1.67\sim-0.12$
$TiO_2 \rightarrow Ti_9O_{17} \rightarrow TiN_xC_yO_{1-x-y} \rightarrow TiN$	$-3.38\sim1.56$	$-1.69\sim2.36$	$-0.12\sim2.88$
$TiO_2 \rightarrow TiN_xC_yO_{1-x-y} \rightarrow TiN$	$1.56 \sim 4$	$2.36 \sim 4$	$2.88\sim4$

^a α₁, α₂ and α₃ are defined as the lg(*P*_{N2}/*P*°) of point i at 800 °C, 900 °C and 1000 °C respectively in Fig. 1. β₁, β₂ and β₃ are defined as the lg(*P*_{N2}/*P*°) of point c at 800 °C, 900 °C and 1000 °C respectively in Fig. 1.



Fig. 2. X-ray diffraction pattern for FeTiO₃:C = 1:3 (carbon powder) over a range of temperatures and time periods in N₂ atmosphere indicated in the figure. ($\blacktriangle - Fe$, $\blacklozenge - TiC$, $\bigstar - TiO_2$, $\blacksquare - Ti_2O_3$, $\blacklozenge - Ti_4O_7$, $\odot - Ti_7O_{13}$, $\bigotimes - Ti_9O_{17}$, $\bigtriangleup - C$, $\Box - FeTiO_3$).

4.1. Effect of reaction temperature on products

According to Fig. 2, the effect of reaction temperature on products can be obtained, as shown in Table 3. It is observed from Table 3 that the main phases in the products are Fe, Ti_9O_{17} , Ti₇O₁₃, Ti₄O₇, Ti₂O₃, and TiO₂ at 800 °C. This indicates that iron can be easily reduced from FeTiO₃ to metallic iron and the reduction rate is very fast, while TiO₂ can be partially reduced to titanium sub-oxides only. However, no TiN is observed in the products at 800 °C, implying that the nitridation of titanium oxide and sub-oxides need to be carried out at higher temperatures. When temperature is elevated to 900 °C, in addition to Fe and titanium oxides, a small amount of TiN begins to form. At 1000 °C, the amount of TiN increases rapidly whereas those of titanium oxides decrease gradually, indicating that the rising of temperature is in favor of the transformation of titanium oxides into TiN. By 1100 °C, only Fe and TiN are present which means that FeTiO₃ has already transformed into TiN completely.

In order to observe the variation of characteristic peak intensity of XRD with reaction temperature clearly, the strongest XRD peak



Fig. 3. The peak intensity of X-ray diffraction pattern of different product phases after microwave-assisted carbothermic reduction–nitridation for 20 min.

intensities of different product phases for reaction time of 20 min as a function of temperature is shown in Fig. 3, where the intensity of the strongest XRD peak of Fe is used as a measure of the relative amounts present. It is obvious that the peak intensity of TiN increases gradually with the rising of reaction temperature whereas those of titanium oxides, such as Ti_9O_{17} , Ti_7O_{13} , Ti_2O_3 , TiO_2 and Ti_4O_7 decrease. Therefore, increasing in temperature is favorable for the formation of TiN.

The lattice parameters of synthesized TiN were calculated from the X-ray diffraction peaks by MDI Jade. The lattice parameter values calculated as a function of temperature is shown in Fig. 4. It is evident that when temperature is elevated from 900 °C to 1000 °C, the lattice parameter of the TiN phase formed in 20 min increases sharply. This can be contributed to the fact that the C atoms dissolution in the interstitial sites in TiN structure result in an increasing of the lattice parameter [28]. By 1100 °C, the lattice parameters decrease for all samples. On the one hand, the constant removal of CO from the system while keeping a constant pressure of N₂ will result in the replacement of C by N in the TiN_{x-} C_{1-x} lattice to form TiN, which is indicated by the decrease in the lattice parameter [30]. On the other hand, the rising of temperature is benefit to the formation of TiN from the predominance diagrams.

The above characteristics in variation of titanium-containing phases can be analyzed by predominance area diagrams of Ti–N–C–O system. It can be seen from Fig. 1 that as the CO partial pressure decreases, TiO₂ will be reduced to Ti_nO_{2n-1} , TiC_yO_{1-y} and TiC successively. These titanium-containing intermediates formed can react with N₂ gas at the same time to form $TiN_xC_yO_{1-x-y}$, TiN_xC_{1-x} and TiN in the presence of carbon. The experimental results from Table 3 show that the main titanium-containing phases of products are TiN, Ti_9O_{1-y} , TiA_2O_3 and Ti_7O_{13} , but none of Ti_3O_5 , TiN_xC_{1-x} , TiC_yO_{1-y} , $TiN_xC_yO_{1-x-y}$ and TiC was observed. This is because the stable region of Ti_3O_5 is very narrow as shown in Fig. 1 and thence Ti_3O_5 is not stable and can be easily nitridized to TiN as the N₂ partial pressure increases. Moreover, the formation of TiN_xC_{1-x} , TiC_yO_{1-y} , $TiN_xC_yO_{1-x-y}$ and TiC need to be carried out

Table 3

Phases observed after microwave-assisted carbothermic reduction-nitridation^a.

Time (min)	Temperature (°C)					
	800	900	1000	1100		
10	-	-	FeTiO ₃ , Fe, TiO ₂ , Ti ₉ O ₁₇	-		
20	Fe, Ti ₉ O ₁₇ , Ti ₇ O ₁₃ , Ti ₂ O ₃ , TiO ₂ , Ti ₄ O ₇	Fe, Ti ₉ O ₁₇ , Ti ₂ O ₃ , TiO ₂ , Ti ₄ O ₇ ,Ti ₇ O ₁₃ , TiN	Fe, TiN, Ti ₉ O ₁₇ , Ti ₄ O ₇ , TiO ₂ , Ti ₂ O ₃ , Ti ₇ O ₁₃ ,	Fe, TiN		
40	-	-	Fe, TiN	Fe, TiN		
60	-	-	Fe, TiN	Fe, TiN		

^a Phases are arranged in a decreasing order of relative diffraction peak intensities.



Fig. 4. Effect of temperature on the lattice parameters of synthesized TiN.



Fig. 5. The peak intensity of X-ray diffraction pattern of different product phases after microwave-assisted carbothermic reduction–nitridation at 1000 °C.

at much lower CO partial pressure. Besides, they will be also transformed rapidly into TiN at higher N_2 partial pressure even though it can be formed.

Based on above experimental results and analysis, the reaction steps for microwave-assisted carbothermic synthesis of TiN–Fe composite from FeTiO₃ and carbon powder are as follows:

 $\begin{array}{l} \text{Step 1: FeTiO}_3 + C = \text{Fe} + \text{TiO}_2 + \text{CO}(g) \\ \text{Step 2: } n\text{TiO}_2 + C = \text{Ti}_n\text{O}_{2n-1} + \text{CO}(g) \quad (2 \leqslant n \leqslant 9) \\ \text{Step 3: Ti}_n\text{O}_{2n-1} + (nx + 2ny + n - 1)\text{C} + \frac{nx}{2}\text{N}_2(g) = n\text{TiN}_x\text{C}_y\text{O}_{1-x-y} + (nx + ny + n - 1)\text{CO}(g)(x + y = 1; x, y \geqslant 0, 2 \leqslant n \leqslant 9) \\ \text{Step 4: TiN}_x\text{C}_y\text{O}_{1-x-y} + \frac{1-x}{2}\text{N}_2(g) + (1 - x - 2y)\text{C} = \text{TiN} + (1 - x - y) \\ \text{CO}(g)(x + y = 1; x, y \geqslant 0) \end{array}$

The overall carbothermal reduction reaction is given as follows:

$$FeTiO_3 + 3C + \frac{1}{2}N_2(g) = Fe + TiN + 3CO(g)$$

4.2. Effect of reaction time on products

In order to observe the characteristics in the variation of peak intensity of XRD as reaction time clearly, the peak intensity of XRD of different product phases as a function of reaction time at 1000 °C is shown in Fig. 5, which shows that when the reaction



Fig. 6. SEM micrographs of samples after microwave-assisted carbothermic reduction–nitridation. (a and b) 1000 °C/40 min, (c and d) 1100 °C/40 min.

time is 10 min, the main phases of products are $FeTiO_3$, Fe, TiO_2 and Ti_9O_{17} . As reaction time is extended to 20 min, in addition to titanium oxides such as Ti_2O_3 , Ti_7O_{13} and Ti_9O_{17} , there is a little amount of TiN in products, while $FeTiO_3$ is disappeared entirely. This implies that $FeTiO_3$ can be easily transformed into metallic Fe and titanium oxides with a fast reaction rate but the nitridation of titanium oxides into TiN is difficult relatively. However, the titanium oxides can be gradually nitridized to TiN as reaction time prolongs. There is no other substance existing except for Fe and TiN when reaction time is 40 min, as shown in Fig. 5. Therefore, FeTiO₃ can be transformed into TiN-Fe composite completely if the temperature is higher than1000 °C and the reaction time is greater than 40 min when microwave heating is used to assist carbothermic reduction-nitridation.

However, FeTiO₃ cannot be completely transformed into TiN-Fe composite when using conventional heating until reaction time exceeds 60 min at 1400 °C [12]. Thus, the microwave heating can significantly lower reaction temperatures and shorten reaction time as compared with conventional heating. This may be mainly attributed to the following microwave-heating characteristics [31,32]. First of all, FeTiO₃ and carbon are good microwave absorption materials. In the microwave heating process, they can be preferentially heated to high temperatures in a short time, and the high temperatures localized within carbon and FeTiO₃ can enhance their reactivity. Secondly, microwave has a large transmission depth to materials which can solve the "cold center" problems associated with conventional heating [33,34]. Therefore, microwave can considerably promote the carbothermic reductionnitridation process of FeTiO₃ due to the localized high temperatures and the large transmission depth.

4.3. Micrographs of products

The micrographs of carbothermic reduction-nitridation products at different temperatures for 40 min are shown in Fig. 6. It is noticed that particles of the products are sub-micrometer sized and uniformly shaped. When the temperature applied is 1000 °C, the microstructure of products is approximately flake (Fig. 6a and b). The size of flakes is increased when temperature is raised to 1100 °C (Fig. 6c and d).

4.4. Acid leaching treatment

In order to obtain pure TiN, acid leaching treatment is used to remove metallic Fe from the TiN-Fe composite prepared at 1000 °C for 60 min in N₂ atmosphere. Figs. 7 and 8 show the XRD patterns and SEM micrograph of samples after leached with 10% HCl aqueous solution at room temperature respectively. It can be seen that purified TiN is obtained with the removal of metallic Fe (Fig. 7). The SEM micrograph reveals that the morphology of TiN particles becomes irregular as compared with those of the samples before leached (Fig. 8).



Fig. 7. X-ray diffraction pattern of products leached with 10% HCl solution at room temperature.



Fig. 8. SEM micrograph of products leached with 10% HCl solution at room temperature.

5. Conclusions

- (1) TiN was successfully synthesized from FeTiO₃ through the microwave-assisted carbothermic reduction-nitridation followed by acid leaching treatment.
- (2) Thermodynamic analysis of Ti-Fe-N-C-O system indicates that titanium and iron oxides can be transformed into TiN–Fe composite by controlling suitable CO and N₂ partial pressure at high temperatures.
- (3) TiN-Fe composite can be prepared from FeTiO₃ by microwave-assisted carbothermic reduction-nitridation at 1000 °C for 40 min. The reaction process for the preparation of TiN-Fe composite from FeTiO₃ and carbon under N₂ atmosphere includes four steps:

Step 1: $FeTiO_3 + C = Fe + TiO_2 + CO(g)$ Step 2: $n\text{TiO}_2 + C = \text{Ti}_nO_{2n-1} + CO(g)$ $(2 \le n \le 9)$ Step 3: $Ti_nO_{2n-1} + (nx + 2ny + n - 1)C + \frac{nx}{2}N_2(g) = nTiN_xC_yO_{1-x-y} + \frac{nx}{2}N_2(g) = nTiN_xO_yO_{1-x-y} + \frac{nx}{2}N_2(g) = nTiN_xO_yO_{1-x-y} + \frac{nx}{2}N_2(g) = nTiN_xO_yO_{1-x-y} + \frac{nx}{2}N_yO_{1-x-y} + \frac{nx}{2}N_yO_{1-x-y} + \frac{nx}{2}N_yO_{1-x-y} + \frac{nx}{2}N_yO_{1-x-y} + \frac{nx}{2}N_yO_{1-x-y}O_{1-x-y} + \frac{nx}{2}N_yO_{1-x-y}$ $(nx + ny + n - 1)CO(g)x + y = 1; x, y \ge 0, 2 \le n \le 9)$ Step 4: TiN_xC_yO_{1-x-y} + $\frac{1-x}{2}$ N₂(g) + (1-x-2y)C = TiN + (1-x-y) $CO(g)x + y = 1; x, y \ge 0$

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