

## The Effect of Reaction Time on the Syntheses of Fe-TiCN Composites from Titanomagnetite Concentrate by Carbothermal Reduction

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**Abstract** — The Fe-TiCN composites were successfully synthesized directly from titanomagnetite concentrate by carbothermal reduction under an air atmosphere at 1500°C. The phase composition and the C/N ratio of the sample were investigated by X-ray diffraction. Studies showed that the C/N ratio of Fe-TiC<sub>1-x</sub>N<sub>x</sub> composites has been remarkably decreased firstly and then tended towards stability with extending the reduction time. With the reaction time extending, the phase evolution sequences followed in the reaction process are: Fe<sub>3</sub>O<sub>4</sub>→Fe; FeTiO<sub>3</sub>→Fe<sub>1.5</sub>Ti<sub>1.5</sub>O<sub>3</sub>→Ti(C,N). The microstructure and element distribution maps of the sample prepared at 1500°C for 30min in air atmosphere were characterized by SEM. The results showed that the TiC<sub>1-x</sub>N<sub>x</sub> particles have the fine sizes about 3 μm and a distinct demarcation line between the Fe phase and the TiCN phase on the surface of the composites. These particles are obviously agglomerated, and the C/N ratio of TiC<sub>1-x</sub>N<sub>x</sub> is 0.4915, x=0.67. The interesting observation is that the V element has been discovered and consistent with the distribution of Ti in the Fe-TiC<sub>1-x</sub>N<sub>x</sub> composites.

**Keywords** — Fe-TiCN; carbothermic reduction; titanomagnetite; composites

### I. INTRODUCTION

Titanium carbonitrides (TiCN) is an attractive material because of its good mechanical and physical properties, such as high hardness, high melting point, and wear and corrosion resistance. Therefore it has been widely used to prepare advanced engineering ceramic-based composites when mixed with binders and other refractory carbides applied in metalworking, electrical and electronic, and refractory industries [1-3]. The most usual materials for binders are Co, Ni and their alloys [4-6]. However, these elements are scarce, expensive. So wider application is limited. For these reasons, there is growing interest in identifying alternative matrixes for cermet and cemented carbides. Researches have been indicated that propose the use of Fe as a metallic matrix and TiC as reinforcement for cermet, as it is non-toxic and cheaper than Co or Ni, with the additional advantage of being able to be hardened by heat treatment. Furthermore, this composite offers the opportunity to use relatively cheap and abundant raw materials [7].

The use of TiCN is preferred to TiC due to its greater hardness and strength, higher thermal conductivity and lower mass gain at high temperatures [8]. It has been reported that Fe-TiCN composite is currently available and produced by powder metallurgy routes and high-energy milling technology. These methods require expensive raw materials, harsh atmosphere and expensive equipment. So many researchers tried to develop low cost preparing processes for Fe-TiCN composites. Carbothermal reduction offers the possibility of an economically attractive production route for Fe-TiCN composite. Several research have been performed using ilmenite as a raw material, for the production of Fe-

TiCN composites by carbothermal reduction in an N<sub>2</sub> [9]. Titanomagnetite concentrate is not only quite cheap but also very rich in China, compared with ilmenite. The preparation of Fe-TiCN directly from titanomagnetite concentrate is very potential. Up to now, the studies on synthesis of Fe-TiCN composites with titanomagnetite/ carbon powder as starting materials in an air atmosphere used widely in industrial production are still rare. The aim of this work is the feasibility of producing Fe-TiCN composites from cheaper materials (titanomagnetite concentrate and carbon powders) via carbothermal reduction in an air atmosphere and the effect of the reduction time on the phase composition, microstructures and the C/N ratio of Fe-TiCN composites were investigated in detail.

### II. METHODOLOGY

The starting materials were titanomagnetite concentrate (Panzhuhua mineral, China) with mean particle size of 90 μm. Its chemical composition is listed in Table 1 and carbon powder (200 μm) with a purity of more than 80% was used as the reducing agent. The mineralogical analysis of the titanomagnetite concentrate was investigated by XRD. The result in Figure.1 indicates that the main crystalline phases of sample are ilmenite (FeTiO<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>).

TABLE I CHEMICAL ANALYSIS OF USED TITANOMAGNETITE CONCENTRATE (WT%)

TFe	FeO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>
56.00	23.49	54.51	10.50	0.58
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	S	CaO	MgO
3.83	1.83	0.257	2.263	2.292

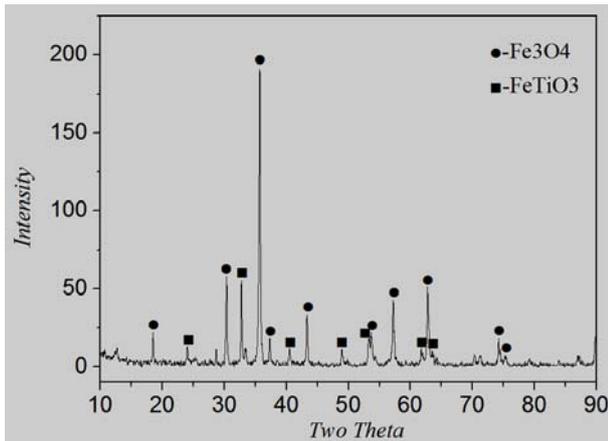


Figure.1 XRD patterns of the titanomagnetite concentrate

Before mixing, all the reagents were dried in an oven at 120°C for 4 h to remove the moisture existed in the raw materials. The samples with vanadium titanomagnetite concentrate and carbon powder were thoroughly mixed and grounded with 4 wt% polyvinyl alcohol (PVA). Then the mixtures were pressed with a pressure of 4 MPa in a closed die to obtain a pellet. The molar ratio of C fixed /O (bonded with Fe and Ti) was fixed at 1.2. The pellets were placed in a crucible which was enclosed in a quartz tube and then subjected to carbothermal reduction. The reduction experiments were carried out in a high temperature box resistance furnace with the following processing parameters: atmosphere-air; temperature-1500°C; time-up to 90min. The evolution of the carbothermal reduction process with time is monitored by XRD analysis with Cu K $\alpha$  radiation, morphological and microstructural analysis by scanning electron microscopy (SEM).

### III. RESULTS AND DISCUSSION

#### A. Phase Evolution as Isothermal Time Changed

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 is shown in Figure.2. It is observed that the main phases of products are Fe<sub>1.5</sub>Ti<sub>0.5</sub>O<sub>3</sub>, Fe, TiCN and MgAl<sub>2</sub>O<sub>4</sub> when the reaction time is 5 min. As reaction time is extended to 10 min, the intensity of Fe<sub>1.5</sub>Ti<sub>0.5</sub>O<sub>3</sub> peak is gradually weakened, and the intensity of Fe, TiCN peak is gradually increased. As the reaction time is extended to 15 min, the intensity of Fe, TiCN peak is remarkably increased, while Fe<sub>1.5</sub>Ti<sub>0.5</sub>O<sub>3</sub> is disappeared entirely. This indicates that the titanomagnetite can be easily reduced to metallic iron, TiCN and the reduction rate is very fast. when the reaction time is from 15min to 30min, the intensity of Fe and TiCN peak continues to be increased, but the increase amplitude was less than in the first 15min. The phase composition and peak intensity of reaction products is remain unchanged when reaction time is greater than 30 min,

which means that titanomagnetite has already been transformed into Fe-TiCN completely and the proper reaction time is 30min at 1500°C.

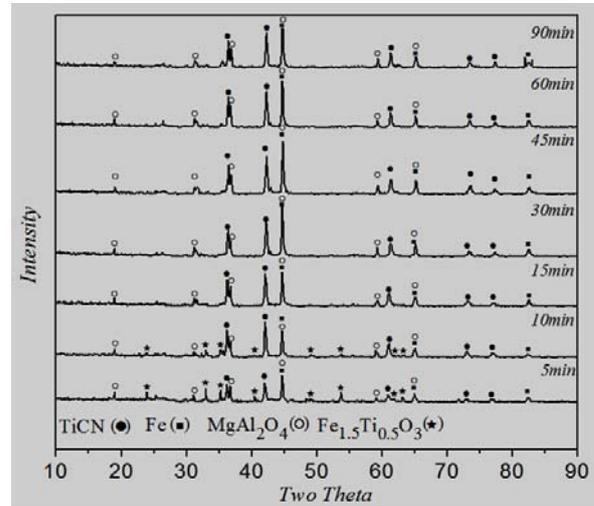
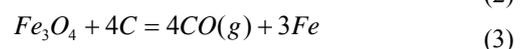
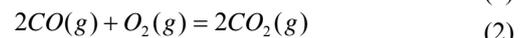
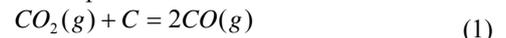


Figure.2 XRD patterns of the samples reduced in air atmosphere, for different reaction times

#### B. The C/N Ratio of TiC<sub>1-x</sub>N<sub>x</sub> Evolution as Isothermal Time Changed

The TiC<sub>1-x</sub>N<sub>x</sub> is a continuous solution of TiC and TiN and the properties of TiC<sub>1-x</sub>N<sub>x</sub> is depend on C/N ratio. Generally, with decreasing C/N ratio, the unit cell parameter of TiC<sub>1-x</sub>N<sub>x</sub> decreased linearly, and the hardness would drop down; yet the toughness would be enhanced on the contrary. So it is necessary to study the C/N ratio of Fe-TiC<sub>1-x</sub>N<sub>x</sub> composites with the different reduction time. The lattice parameter of the TiC<sub>1-x</sub>N<sub>x</sub> solid solution was a linear function of the composition and fulfilled Vegard's law, which can be calculated from the X-ray diffraction peaks by MDI Jade (Figure.2). In accordance with Vegard's rule, the C/N ratio of TiC<sub>1-x</sub>N<sub>x</sub> calculated as a function of reaction time is shown in Figure.3.

Some researchers observed that synthesis of TiCN from TiO<sub>2</sub> by carbothermal reduction, which the C/N of TiCN depends on both N<sub>2</sub> and CO partial pressures in reaction system[10]. In order to enhance Nitriding reaction, the experiments flowing nitrogen atmosphere, which constant removals CO from the system while keeping a constant pressure of N<sub>2</sub> will result in the replacement of C by N in the TiC<sub>1-x</sub>N<sub>x</sub>. But in this study, the experiments are carried out in air atmosphere and the main reaction in experimental temperature can be expressed as follows:



In the early stage (up to 5min reaction time), the solid-solid reaction and between Fe<sub>3</sub>O<sub>4</sub>, FeTiO<sub>3</sub> and the

surrounding carbon particles and the Combusting reaction of CO and Boudouard reaction happened at the same time at 1500°C in an air atmosphere. When the gaseous envelope of CO was formed around the reactants, the CO can quickly diffuse to contact Fe<sub>3</sub>O<sub>4</sub> and react, which can be used to explain well that the reaction rate is so much fast. In addition, the high PCO/PN<sub>2</sub> ratio is not favorable for nitriding reaction, which lead to a high C/N ratio with respect to the initial state (Figure.3). During the second period (extending to about 30min), the CO was constantly consumed from the system by the Combusting reaction because the C content is fixed in the reactant, which means the PCO/PN<sub>2</sub> ratio constantly decrease and the C/N ratio of the composites was lower (Figure.3). With the reaction time further extending, the metal Fe liquid phase appeared and that hindered the transmission of N<sub>2</sub> during the reaction process, therefore the C/N ratio of the composites was not changed (Fig.3). When the reaction time is 30min at 1500°C, the C/N ratio of TiC<sub>1-x</sub>N<sub>x</sub> is 0.4915, x=0.67.

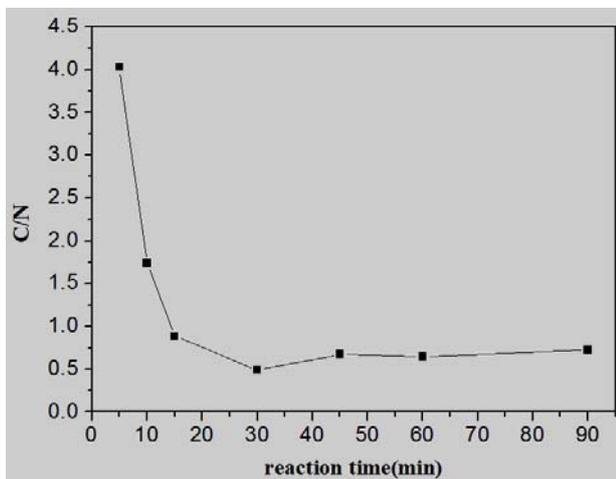


Figure.3 The relationship between the C/N ratio and the reaction time

C. Characterization by SEM

Figure.4 shows microstructure and the Fe, Ti, N and C distribution of the composites after 30min of the carbothermal reduction process in air atmosphere. It is noticed that a distinct demarcation line between the Fe phase and the TiCN phase on the surface of the composites, and the particles have the characterization of liquid-phase sintering. Figure.5 shows the SEM micrographs and the Fe, Ti, V, Al and Mg distribution of (taken in BSE mode) samples after carbothermal reduction for 30min in air atmosphere. The MgAl<sub>2</sub>O<sub>4</sub> is dark, TiC is gray, and the Fe phase is brightly colored in the images, and it illustrates that the TiCN particles have the fine sizes around 3 μm and these particles are obviously agglomerated. It is noteworthy that the V element has been discovered and consistent with the distribution of Ti in the composites, which means that the V of titanomagnetite is reduced to VC. The VC have much high solubility in the binder phase of TiCN-based cermet, which leading to an improved plasticity of the rim and

enhanced bending strength, and the others in the cermet would disperse at the interface and inhibit the core growth, thus resulting in a higher hardness.

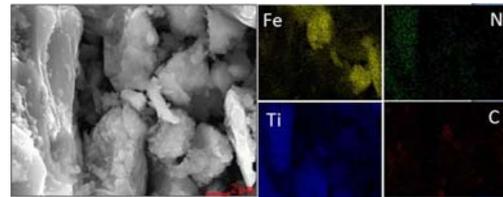


Figure.4 SEM images and element distribution maps of samples with the reduction time is 30min at 1500°C

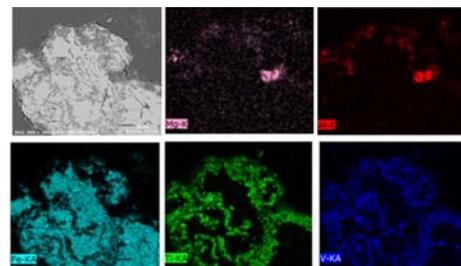


Figure.5 BSE images and element distribution maps of samples with the reduction time is 30min at 1500°C

IV. CONCLUSION

The Fe–TiCN composites from titanomagnetite concentrate and carbon powders were successfully prepared via carbothermal reduction in air atmosphere. When the reaction time is 5 min, the main phases of products are Fe<sub>1.5</sub>Ti<sub>0.5</sub>O<sub>3</sub>, Fe, TiCN and MgAl<sub>2</sub>O<sub>4</sub>. The intensity of Fe, TiCN peak is gradually increased with the reaction time extend, while the intensity of Fe<sub>1.5</sub>Ti<sub>0.5</sub>O<sub>3</sub> peak is weakened and disappeared entirely. The C/N ratio of TiCN is decreased clearly in the first 30min and then, it remains constant. The titanomagnetite has been transformed into Fe–TiCN completely when the reaction time is 30min at 1500°C. Under these conditions, the TiC<sub>1-x</sub>N<sub>x</sub> particles have the fine sizes about 3 μm and these particles are obviously agglomerated, and the C/N ratio of TiC<sub>1-x</sub>N<sub>x</sub> is 0.4915, x=0.67. The interesting observation is that the V element has been discovered and consistent with the distribution of Ti in the composites.

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