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Syntheses of Fe–TiC nanocomposite from ilmenite concentrate via microwave heating

MANSOUR RAZAVI, MOHAMMAD REZA RAHIMIPOUR*, TOORAJ EBADZADEH and SEYED SALMAN RAZAVI TOUSI

Materials and Energy Research Centre, P.O. Box 14155-4777, Tehran, Iran

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Abstract. **In this paper, the possibility of production of Fe–TiC nanocomposite as a useful ceramic, from ilmenite concentrate, aluminum powder and carbon black has been investigated. Different amounts of $FeTiO_3$, carbon black and Al powder were activated by a high-energy ball mill. Then the mixtures were synthesized by microwave heating at various times. The results of XRD investigation indicated that TiC has been synthesized within 5–10 min treatment microwave time. Moreover, it was found that by increasing the aluminum content, the Fe_2O_3 phase was replaced by SiC and Al_2O_3. In addition, from the broadening of the diffraction lines in the XRD patterns analysis, it was concluded that the TiC crystallites are nano-sized. Also, it was found that the existence of Al lead to increased grain size and decrease of the strain in the process.**

Keywords. **Nano-crystal; microwave sintering; mechanically activated; titanium carbide; ilmenite.**

1. Introduction

The Fe–TiC composite is one of the special composites that was first studied in the 1950s (Jiang *et al* 1997). This material has different trade names such as ferrotic, TiC alloy and ferrotitanit and the name ferrotic is more famous than the other two (Terry and Chinyamakobvu 1992; Das *et al* 2002). Matrix of this composite is mostly composed of tool steel, low and high alloy steel, stainless steel, aged martensite steel, cast iron etc (Cherysanthou *et al* 1996; Rai *et al* 1999) and accordingly hardness varied from 55–70 HRC (Panchal *et al* 1990). Moreover, wear resistance of Fe–TiC is 2–3 times more than tool steel and 20% higher than WC–Co. Machinability of this composite is 50% better than tool steel due to its lower density (Rai *et al* 1999). Although there are many other matrixes with lower densities, the iron matrix composites are still favourable in industries because of their low cost and popularity (Das *et al* 2002).

Microwave sintering is one of the heating methods which can be used for synthesizing of Fe–TiC composite. Microwave heating offers the potential of an enhanced sintering process along with a decreased densification temperature as well as a shortened processing time. Moreover, a smaller grain size can be obtained via microwave processing due to the higher heating rate and shorter sintering cycles. In microwave processing, energy is directly transferred to the material through the interaction of electromagnetic waves with molecules which leads to heating and consequently synthesizing the composite (Clark *et al* 1991; Ebadzadeh and Valefi 2008).

In this paper, the possibility of synthesis of Fe–TiC composite from low-cost raw materials, using microwave sintering technique will be investigated.

2. Experimental

In this work, powder mixtures of $FeTiO_3$, C and Al have been examined. The $FeTiO_3$ used here for synthesizing Fe–TiC had been prepared from Kahnooj ilmenite concentrate with particle size under 150 mesh. Table 1 gives a summary of the chemical composition of ilmenite concentrate. The XRD pattern of this powder showed $FeTiO_3$ as the only crystalline phase which exists in the mixture (figure 1). Carbon black with a particle size under 250 mesh was used as the source of carbon. XRD analysis expressed that the carbon black was amorphous. Moreover, 99·9% purity aluminum powder with particle size under 250 mesh was used. All the input materials with stoichiometric ratio were mixed (according to following reaction) with 5, 10 and 15 wt% Al and milled for 3 h.

$$FeTiO_3 + 4C = Fe + TiC + 3CO.$$

The applied ball mill was of planetary type which was classified as high-energy ball mills. The ball to powder weight ratio was 10 : 1 in all the experiments. Three similar balls with a diameter of 20 mm were utilized. Also, in order to protect the materials from oxidation, argon gas with a purity of 99·9999% and pressure of 2·5 bar was charged in the container cylinder of raw materials. More-

*Author for correspondence (m-rahimi@merc.ac.ir)

Table 1. Chemical analysis of used ilmenite concentrate.

Element	TiO_2	FeO	Fe_2O_3	Al_2O_3	MnO	MgO	SiO_2	CaO	V_2O_5	Cr_2O_3	P_2O_5	Other
Weight percent	47·4	34·2	10·6	1·3	1·7	1	2	1	0·3	0·03	0·15	Balance

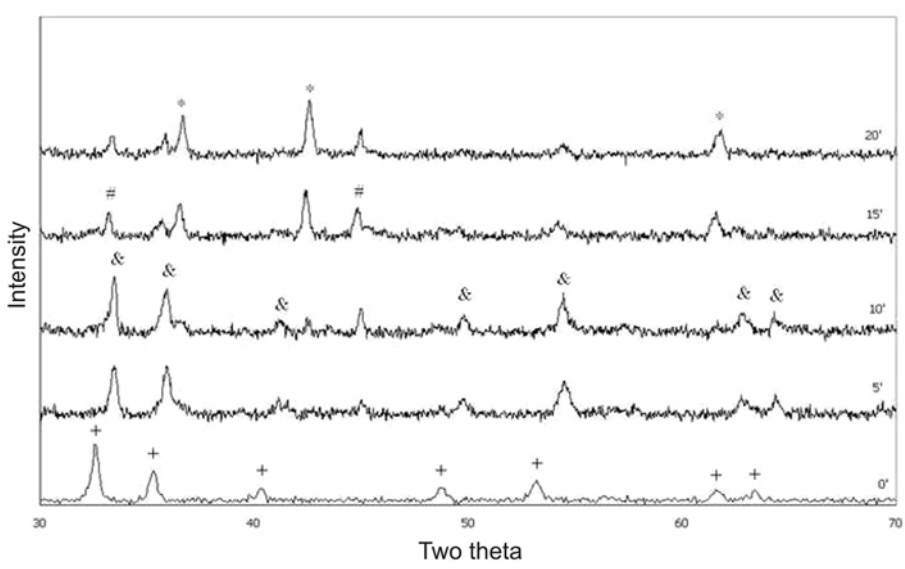

Figure 1. The X-ray diffraction patterns of the obtained specimens containing $FeTiO_3$–C which was heated in microwave for 5, 10, 15 and 20 min: (TiC (*), TiO (#), Fe_2O_3 (&), $FeTiO_3$ (+)).

over, the dick samples with 20 mm diameter and 5 mm thickness were produced in a steel die using a load of 1000 kg.f.

Then the samples were sintered in a domestic microwave with 2·45 GHz frequency and 900 W power and compared with those sintered through the conventional heating. A SiC crucible was used as a susceptor due to its efficient absorbance of microwave energy because of its high loss factor (Zhao *et al* 2001). The SiC crucible indirectly heats the samples to a high enough temperature and improves the sinterability of the samples. All runs were made by fast heating up to a maximum temperature which was measured using a *R*-type thermocouple placed in contact with the sample surface quickly (2 s) after turning off the power and then samples were cooled down to room temperature.

In order to detect the type of synthesized phases and formed components, XRD analysis (Siemens model) with voltage and current of 30 kV and 25 mA, respectively and CuKα radiation (λ = 1·54 Å), was carried out. In addition, the crystallite size and strain were evaluated through Williamson–Hall method by the following equation:

$$b\cos\theta = \frac{0{\cdot}9\lambda}{d} + 2\eta\sin\theta,$$

where b is full width of peak at half intensity (rad.), θ the position of peak in the pattern (rad.), λ the wavelength of X-ray (nm), η micro strain in the powder (Williamson and Hall 1953). The microstructure of samples was examined using a transmission electron microscope (Philips model) with a voltage of 25 kV.

3. Results and discussion

3.1 *$FeTiO_3$–C binary system*

The X-ray diffraction patterns obtained from specimens containing ilmenite concentrate and carbon black which was heated in microwave for 5, 10, 15 and 20 min are illustrated in figure 1. As it can be seen in the beginning only the $FeTiO_3$ peaks can be observed and there are no peaks from carbon because the carbon black used in the experiment had amorphous structure. Even if this carbon is not amorphous, it would have been very difficult to identify its peaks due to significant differences between the mass absorption coefficients of Ti and C, which are 208 m^2/g and 4·6 m^2/g, respectively (Lohse *et al* 2005).

However, as the heating time rose to 5 min, iron and titanium oxides appeared. Because of the thermodynamic stability, these phases will remain even if the heating times increase. After the time of 10 min, weak peaks of TiC appear which by increasing the time it will be increased too. Also at the maximum of heating time

(20 min), the $FeTiO_3$ peaks are completely replaced by TiC, iron oxide and titanium oxide. Das *et al* (2002) reported that after the synthesis after 1 h heating of $FeTiO_3$–C mixture in furnace under flowing argon atmosphere at 1300–1600°C, TiC can be formed. In the present work, TiC was produced in short time but the existence of iron and titanium oxide as undesired phases were yet unpreventable.

The equilibrium formation temperature of TiC from $FeTiO_3$ can be calculated theoretically. Using the information as broughtout in table 2, the Gibbs free energy function and the Ellingham–Richardson diagram of the formation reaction of TiC from C and $FeTiO_3$ can be calculated (Gaskell 1995). The amount of this energy can be determined according to the following relations

$$\Delta G = 722438 - 276T - 44T\ln T + 0{\cdot}08T^2 - \frac{1016000}{T}$$

$$298 < T < 800,$$

$$\Delta G = 949304 - 2355T + 246T\ln T - 0{\cdot}05T^2 - \frac{32122500}{T}$$

$$800 < T < 1000,$$

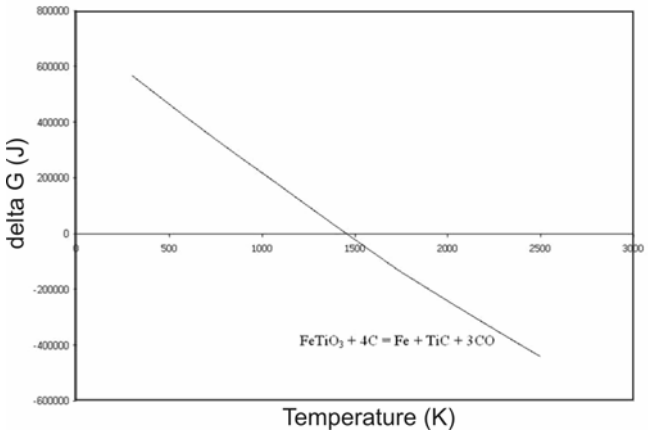

Figure 2. The Ellingham–Richardson diagram for the formation reaction of TiC from C and $FeTiO_3$.

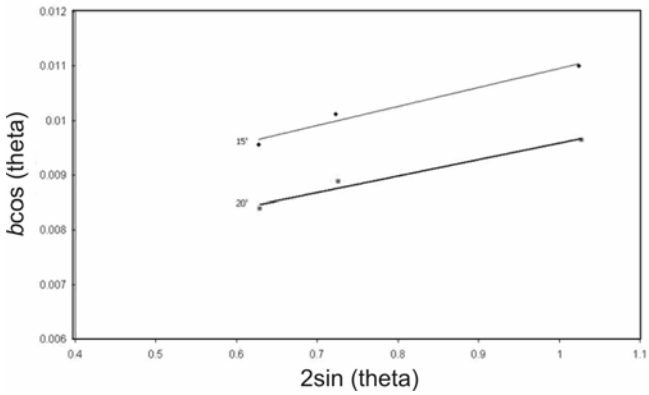

Figure 3. Williamson–Hall diagram of the $FeTiO_3$–C system for specimens heated in microwave for 15 and 20 min.

$$\Delta G = 468576 - 314T + 48T\ln T - 0{\cdot}27T^2 - \frac{1161000}{T}$$

$$1000 < T < 1042,$$

$$\Delta G = -278620 + 13083T - 1962T\ln T + 0{\cdot}97T^2 - \frac{1161000}{T}$$

$$1042 < T < 1060,$$

$$\Delta G = 1462867 - 4777T + 545T\ln T - 0{\cdot}09T^2 - \frac{146777512}{T}$$

$$1060 < T < 1100,$$

$$\Delta G = 1487571 - 5391T + 643T\ln T - 0{\cdot}16T^2 - \frac{152742512}{T}$$

$$1100 < T < 1184,$$

$$\Delta G = 777104 - 941T + 57T\ln T - 0{\cdot}002T^2 - \frac{7137000}{T}$$

$$1184 < T < 1665,$$

$$\Delta G = 774687 - 934T + 56T\ln T - 0{\cdot}002T^2 - \frac{7137000}{T}$$

$$1665 < T < 1740,$$

$$\Delta G = 798760 - 1548T + 138T\ln T - 0{\cdot}01T^2 - \frac{6135000}{T}$$

$$1740 < T < 1809,$$

$$\Delta G = 790083 - 1392T + 117T\ln T - 0{\cdot}01T^2 - \frac{6135000}{T}$$

$$1809 < T.$$

In these relations, temperature and energy are in Kelvin and Joule, respectively. The Ellingham–Richardson diagram of formation reaction of TiC from C and $FeTiO_3$ is plotted in figure 2. According to this diagram the equilibrium formation temperature of TiC from $FeTiO_3$ is around 1454°C.

Mechanical activation of raw materials and higher heating rate using microwave energy could decrease the formation temperature. The maximum temperature which had been shown by thermocouple was 1205 ± 5°C.

Figure 3 shows Williamson–Hall diagram of the system and the mean size of the grains while the strain percentages are shown in table 3. In this table, y represents $b\cos\theta$ and x represents $2\sin\theta$ in Williamson–Hall equation. Hence a as the slope represents the strain (η) and b as the y-intercept identifies $0{\cdot}9\lambda/d$ from which the grain sizes (d) can be calculated. These results indicated that the grain size of TiC is in the nanometer scale (18–21 nm). Since the TiC grain size is very fine, the separated TiC particles from other elements by some methods like

Table 2. Thermodynamic data.

Substance	S_{298} (J/deg.mol)	$-\Delta H$ (kJ/mol)	T(K)	$C_p = A + BT + C/T^2$ (J/deg.mol)			H_t (kJ/mol)
				A	$B \times 10^3$	$C \times 10^{-5}$	
C	5·7	0	298	0·11	38·94	–1·48	–
			1100	24·43	0·44	–31·63	–
Fe	27·3	0	298	28·18	–7·32	–2·9	–
$FeTiO_3$	105·9	1237·6	298	116·61	18·24	–20·04	–
			1740	199·16	–	–	90·8
TiC	24·7	184·5	298	48·43	3·16	–1·36	–

Table 3. The mean size of the particles and the strain caused by milling and microwave heating in $FeTiO_3$–C system (η: strain, d: grain size, R^2: regression coefficient).

Time (min)	$b\cos\theta = a(2\sin\theta) + b$		d_{TiC} (nm)	η_{TiC} (%)	R^2
	a	b			
15	0·0035	0·0075	18·49	0·35	0·9770
20	0·0030	0·0066	21·01	0·30	0·9758

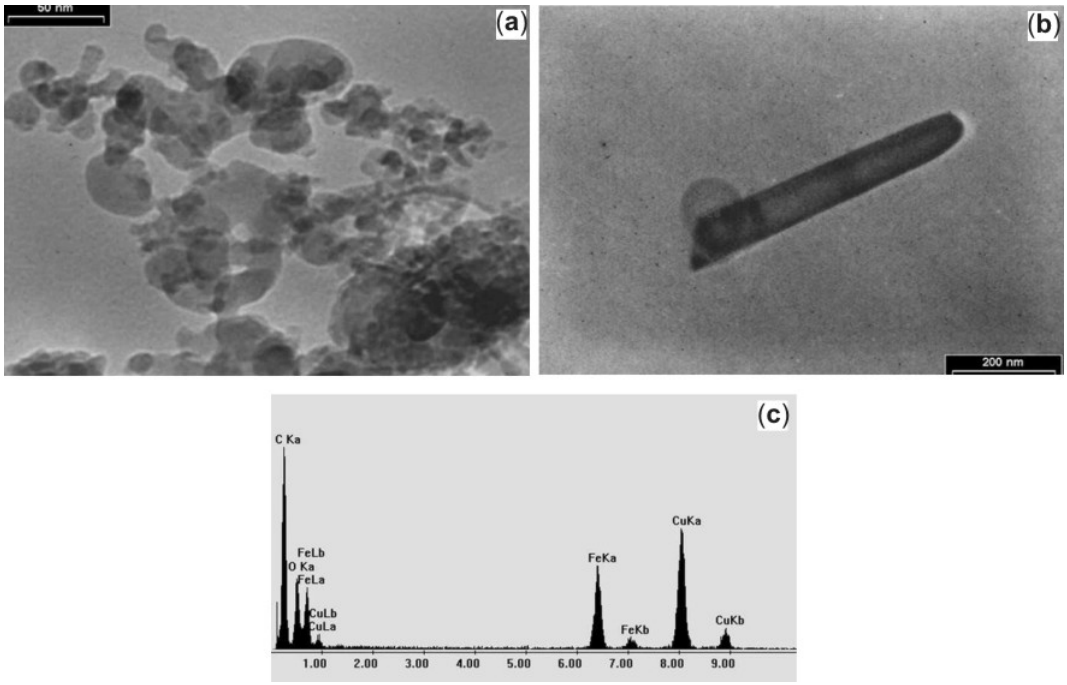

Figure 4. (**a**, **b**) The TEM microstructures of sample synthesized at 20 min in $FeTiO_3$–C and (**c**) EDS of the marked point in sample b.

leaching can be used as reinforcement for increasing the matrix properties. From table 3, as it was also expected the increase of synthesis heating time increases grain size and consequently decreases strain.

The TEM microstructure of sample synthesized at 20 min is presented in figure 4. This micrograph also confirms the nanometer scale of the particles. Also it confirms the results of Williamson–Hall method. In figure 4b a typical tube like particle is observed. The EDS of these particles indicated that these phases are Fe_2O_3 which were grown as tube shape during the process.

3.2 *$FeTiO_3$–C–Al ternary system*

It is expected that addition of aluminum powder as a reduction agent to previous system ($FeTiO_3$–C) can reduce the amount of undesired phases. Using a primary mixture containing Al and metal oxides lead the aluminothermy

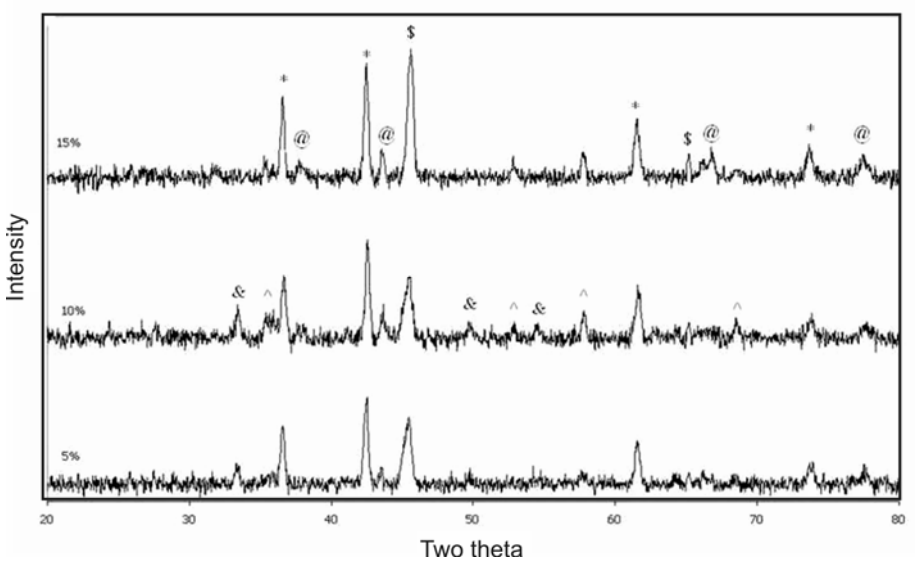

Figure 5. X-ray diffraction patterns of the $FeTiO_3$–C–Al ternary system that was heated in microwave furnace for 20 min with 5, 10 and 15%wt Al (TiC (*), Fe ($), SiC (@), Al_2O_3 (^), Fe_2O_3 (&)).

Table 4. The mean size of the particles and the strain caused by milling and microwave heating in $FeTiO_3$–C–Al system (η: strain, d: grain size, R^2: regression coefficient).

	$b\cos\theta = a(2\sin\theta) + b$				
Weight percent of Al	a	b	d_{TiC} (nm)	η_{TiC} (%)	R^2
5	0·0018	0·0049	28·29	0·18	0·9716
10	0·0014	0·0040	34·66	0·14	0·9459
15	0·0014	0·0038	36·49	0·14	0·9928

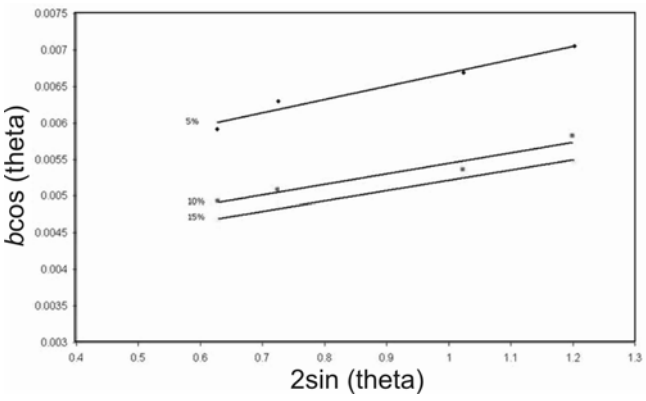

Figure 6. Williamson–Hall diagram of the $FeTiO_3$–C–Al system.

reaction to occur which produces the high energy for completing the reactions. The X-ray diffraction patterns of this ternary system which were heat treated in microwave furnace for 20 min are shown in figure 5.

By adding aluminum to the mixture of $FeTiO_3$ and C, the TiC is produced containing Fe, aluminum and iron oxides. But by increasing aluminum content, Fe_2O_3 peaks were replaced by SiC and Al_2O_3. Also, Si purity in ilmenite can be the source for the formation of SiC phase in the product. The existence of these phases can improve the mechanical properties of matrix and could be used in many applications such as master alloys, coating and sintered bulk parts (Ahmad and Pan 2008).

Moreover, figure 6 shows Williamson–Hall diagram of the system. The mean size of the grains and the strain percentages are presented in table 4. These results confirm that the grain size of TiC is in nanometer scale (around 28–36 nm). Thus the production of ferrotic composite with reinforced nano-scale is possible.

It can be considered that the increase of aluminum amount lead to increase of grain size and decreases the strain which can be related to the exothermic reaction of aluminum with metal oxides. This is the reason for higher grain size of the latter composite with respect to the previous system ($FeTiO_3$–C).

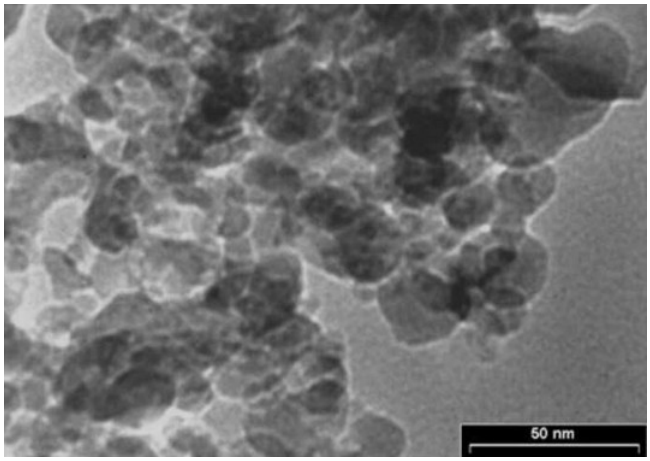

Figure 7. The TEM micrograph of sample synthesized with 10%wt Al.

In addition, the TEM micrograph of sample synthesized with 10%wt aluminum is shown in figure 7. In this, sample tube particles are not observed which indicated Fe_2O_3 were replaced by other phases.

4. Conclusions

(I) Fe–TiC nanocomposite was successfully prepared from ilmenite concentrate, carbon black and aluminum via microwave heating.
(II) Aluminum removed the undesirable phases in the ilmenite and carbon mixture and produced the Fe–TiC–SiC–Al_2O_3 hybrid composite.
(III) The produced TiC crystallite sizes are in the range of nanometer (18–36 nm) and raising the heating time and aluminum amount caused the increase of the grain size and strain.
(IV) Mechanical activation and higher heating rate with microwave decreased the formation temperature.

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