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Short communication

Effect of mechanical activation on syntheses temperature of TiC reinforced iron-based nano-composite from ilmenite concentrate

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Abstract

In this research the possibility of producing Fe–TiC from ilmenite concentrate and carbon black using mechanically activated sintering has been investigated. Ilmenite and carbon black were placed in a planetary ball mill and sampled after different milling times. The activated powders were synthesized at different temperatures in an atmosphere control tube furnace. Studies showed that synthesizing temperature has been remarkably decreased by increasing the milling time. Also it was seen from the width of X-ray patterns peaks that the size of produced TiC crystals is in the order of nanometer. Furthermore the lattice parameter had deviated slightly from the standard size.

Keywords: Nano-crystal; Mechanical activated; Titanium carbide; Ilmenite

1. Introduction

Titanium carbide bounded by iron is a unique metal matrix composite. Its special properties such as strength retained at elevated temperature, good machinability, high wear resistance and mechanical properties and suitable oxidation and corrosion resistance. Furthermore, this composite offers the opportunity to use relatively cheap and abundant raw materials [1–9]. The reinforcement of this composite (TiC) is particularly attractive, because it has high hardness and stiffness, low density, high melting point (3100 °C), desirable properties of corrosion resistance, relatively high thermal and electrical conductivity and chemical stability with iron-based matrices [10–12]. Fe–TiC composite is currently available and produced by powder metallurgy routes involving the addition of TiC powders to iron alloy powders. Besides conventional melting and casting, carbothermic reduction, combustion synthesis, aluminothermic reduction, electron beam radiation, laser surface melting and plasma spray synthesis process are reported for production of this composite [1,13–25].

Recently, the mechanically activated sintering (MSA) process has attracted much interest. Mechanical activation of reactants through high-energy milling can excite processes all of which act as driving forces in secondary processing (heat treating for reaction) of primitive materials. At present, this method exhibits a wide range of potential applications [26]. Therefore, they have been comprehensively studied by many investigators, working on extractive metallurgy, materials synthesis and production of nano-crystalline and amorphous materials [27–33].

The aim of this work is the feasibility of producing Fe–TiC composite from cheaper materials (ilmenite concentrate and carbon black) via mechanical activated sintering and the effect of parameters on the formation of this material.

2. Experimental

In this work, powder mixtures of $FeTiO_3$ and C have been examined. The $FeTiO_3$ used in this research 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 exist in the mixture. 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. All

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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	47.40	34.21	10.61	1.33	1.72	1.03	2.00	1.11	0.34	0.03	0.15	0.07

the input materials with stoichiometric ratio were mixed according to the following reaction:

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

The ball mill used was the planetary type which is classified as high-energy ball mills. The weight ratio of ball to the powder was 10:1 in all the experiments. Three similar balls with the diameter of 20 mm were utilized. Also, in order to protect the materials from oxidation, argon gas with the purity of 99.9999% and pressure of 2.5 bar was charged in the container cylinder of raw materials. After evaluation of the milled powders, for completion of reactions and also investigating the milling effect on the activated materials and TiC synthesizing temperature, heat treatment was performed. Two samples, one without milling and the other with the longest milling time were selected and heat treated. Heat treatment was performed in an atmosphere control tube furnace. Disk samples with 20 mm diameter and 5 mm thickness were produced in a steel die using load of 1000 kg f. To prevent the specimens from oxidation and undesired reactions, argon with the flow of 1.9–2.2 l/min was used. To decrease the oxygen impurity in argon gas, argon was passed through copper wire and titanium components which had a temperature about 200 °C before entering the furnace. Heating rate was constant and equal to 10 °C/min. The samples were held in furnace at 1000 °C, 1250 °C and 1500 °C and then cooled in furnace to room temperature. The holding time was 1 h at the maximum temperature. In order to detect the type of synthesized phases and components, XRD analysis with the voltage and current of 30 kV and 25 mA respectively and Cu Kα radiation ($\lambda = 1.54$ Å) was carried out. The crystallite size and strain of system were calculated from the width of XRD pattern peaks through Williamson–Hall [34] method. Also, for investigation the influence of milling on lattice parameter could be considered using Nelson–Riley [35] method. The lattice parameter of TiC is 0.4327 nm in accordance to file of 73-0472 of the international center for diffraction date (JCPDS-ICDD 2000).

3. Results and discussion

XRD patterns of the samples containing $FeTiO_3$ and C which have been milled for 20 h and 50 h were shown in Fig. 1a. Hence the detectable phases were $FeTiO_3$ and $FeTiO_3$ with titanium oxide (Ti_3O_5) for 20 h and 50 h milling respectively. Therefore $FeTiO_3$ cannot be reduced by C even with long milling time. The only significant feature which happened during milling was a small broadening of the peaks and reduction of their intensity which could mean that phases had became finer.

X-ray diffraction of the heat treated samples in two conditions of non-milling and after 50 h milling is shown in Fig. 1b and c. In non-milled samples which have been heat treated at 1000 °C the sharp peaks were corresponded to titanium and iron oxides, although existence of weak peaks of Fe was not discredited certainly (Fig. 1b). Increase of the heat treatment temperature to 1250 °C results in the formation of TiO and Ti_2O_3 which are titanium oxides with lower degree of oxygen in comparison with TiO_2. Strong TiC peaks can be

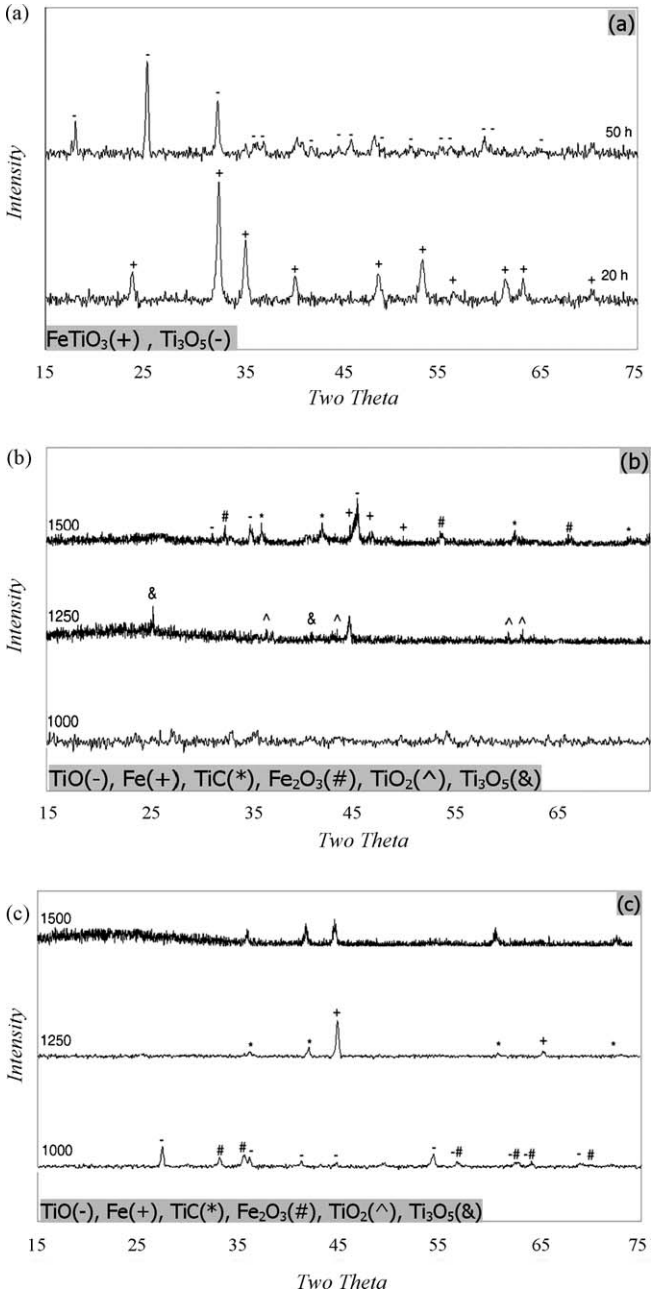

Fig. 1. XRD patterns of (a) milled samples, (b) heat treated specimens without milling and (c) heat treated specimens after 50 h of milling.

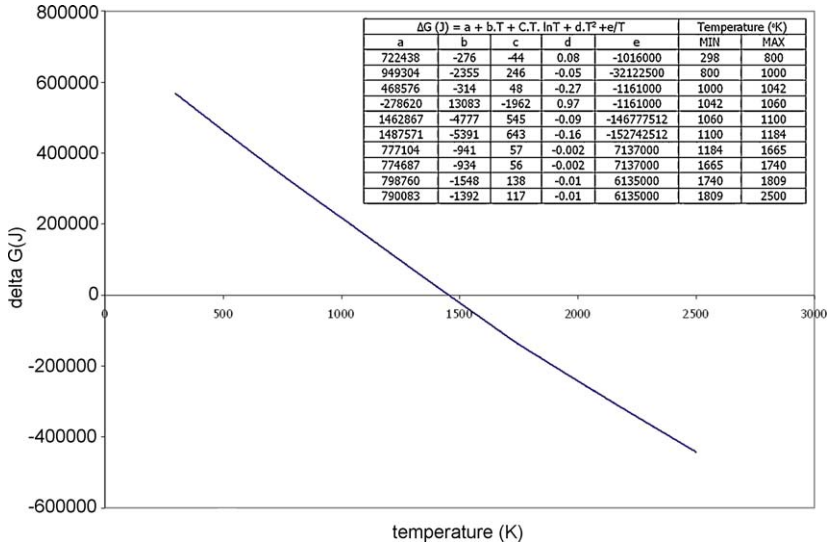

Fig. 2. The Ellingham–Richardson diagram for the formation reaction of TiC from C and $FeTiO_3$.

observed by increasing the temperature up to 1500 °C with Fe and titanium and iron oxides peaks. Hence in this condition TiC with Fe and some undesired phases (titanium and iron oxides) was formed between 1250 °C and 1500 °C.

In milled samples titanium and iron oxides and some peaks of Fe were observed which do not have remarkable differences with no-milled specimens. The increase of the heat treatment temperature to 1250 °C resulted in the formation of TiC with Fe. Stronger TiC peaks can be observed by increasing the temperature up to 1500 °C (Fig. 1c). Milling caused that the $FeTiO_3$–C powder was activated hence synthesizing temperature reduced (1000–1250 °C).

In this system, the reaction which can be supposed for the formation of TiC and Fe from $FeTiO_3$ and C is

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

Therefore the production of Fe–TiC composite via milling and then heat treatment between 1000 °C and 1250 °C is possible. This powder can be used as master alloys in the casting industry [36].

The equilibrium formation temperature of TiC from $FeTiO_3$ can be calculated theoretically. The Gibbs free energy function and the plot of the Ellingham–Richardson diagram of the formation reaction of TiC from C and $FeTiO_3$ can be calculated [37]. The Ellingham–Richardson diagram of formation reaction of TiC from C and $FeTiO_3$ with the amount of this energy is shown in Fig. 2. According to this diagram this reaction is endothermic and the equilibrium formation temperature of TiC from $FeTiO_3$ is around 1454 °C. But in this research milling operation has reduced the formation temperature to 1000–1250 °C.

The mean grain size of produced TiC powder and amount of stress in the system were determined. The results are presented in Table 2. As it can be seen, the size of TiC crystals is about nanometer and increase of the heat treatment temperature leads the crystals to grow and reduce the strain.

The lattice parameter is calculated using Nelson–Riley equation. The quantity that can be calculated is 0.4301 nm and 0.4317 nm for temperature of 1250 °C and 1500 °C respectively and the amount of deviation from standard state of TiC is 0.0026 nm and 0.0010 nm. This deviation can be related to increase in the amount of strain, formation of TiC with non-stoichiometric ratio and lack of calibration of instruments [38].

Table 2
Mean grain size and stress amount of $FeTiO_3$–C mixture milled for 50 h and heat treated at 1250 °C and 1500 °C based on Williamson–Hall equation.

Temperature (°C)	$y = ax + b$		d_{TiC} (nm)	η_{TiC} (%)	R^2
	a	B			
1250	0.0013	0.0053	26	0.53	0.83
1500	0.0007	0.0047	39	0.07	0.82

4. Conclusion

(1) TiC powder and Fe–TiC composite were successfully prepared from ilmenite concentrate and carbon black via mechanical activation.
(2) Mechanical activation reduced the temperature of formation of Fe–TiC composite from 1250–1500 °C to 1000–1250 °C.
(3) Despite performing heat treatment on milled samples, TiC crystallite size was in nanometer order (about 26–40 nm).
(4) Milling the mixture of powders resulted in the deviation of TiC lattice parameter from standard state.

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