Development of an Alternate Route Based on Mechanochemistry towards the Synthesis of Nanostructured TiC

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Industrial grade ferrotitanium (Fe–Ti) was used for the first time as the raw material to synthesize TiC. Mixtures of Fe–Ti and graphite were milled in a planetary ball mill for varying durations between 10 h and 40 h. The milled mixtures were subsequently heat treated at 1000°C for 15 min. The powder mixtures were characterized by using XRD and SEM-EDAX. In an attempt to purify the TiC, the milled and heat treated powder products were leached with dilute HCl. The XRD patterns of as milled heat treated powders indicated formation of crystalline TiC. SEM images also indicated grain refinement even though agglomeration to some extent was noticed. The mechanochemical route coupled with leaching thus offers a successful way to synthesize TiC from a cheap source that has not been attempted before.

KEY WORDS: ball milling; Fe–Ti; nanostructured material; TiC; synthesis.

1. Introduction

Titanium carbide is widely used as wear resistant tools, grinding wheels and aerospace materials due to its extremely high melting temperature, high hardness, high chemical resistance to oxidizing atmosphere, and good electrical conductivity. The bulk production of materials containing TiC as a component has been made possible by the extensive application of TiC powder consolidation using powder metallurgy techniques.1,2) TiC can be synthesized by direct chemical reaction between titanium and carbon under vacuum at high temperature. This method, however, is rather expensive because of the high cost of elemental Ti and because it is an energy intensive process.3) TiC is commercially produced by the carbothermal reduction of TiO2 using carbon black as shown below:4)

$$\text{TiO}_2(s) + 3\text{C}(s) = \text{TiC}(s) + 2\text{CO} \ (g)$$ ................. (1)

The synthesis of TiC by means of carbothermal reduction of TiO2, however, requires high temperature (1700°C–2100°C) and a long reaction time (10 h–24 h). Since the reactants (TiO2 and carbon) both react in solid states, the reaction rate is rather slow.5) Nanostructured TiC can be synthesized by methods such as liquid-magnesium reduction of vaporized mixture of TiCl4 and CCl4 solution. The corresponding reaction takes place as follows:1)

$$\text{TiCl}_4 \ (g) + \text{CCl}_4 \ (g) + 4\text{Mg} \ (g) = \text{TiC}(s) + 4\text{MgCl}_2 \ (l)$$ ......................................................... (2)

Thermal plasma has also been used for the synthesis of TiC using titanium and methane as starting materials:4)

$$\text{Ti} \ (s) + \text{CH}_4 \ (g) = \text{TiC} \ (s) + 2\text{H}_2 \ (g)$$ ................. (3)

In an attempt to synthesize TiC at lower temperature thus consuming less energy as well as to avoid grain growth, mechanochemical route was adopted by using Fe–Ti as the substitute of pure titanium powder and graphite as the raw materials. Use of Fe–Ti in the synthesis of TiC has not been reported so far by any other researcher. Fe–Ti being considerably cheaper than pure Ti with a higher chemical stability, its successful use promises to open up a cheaper alternate route towards TiC synthesis. In addition to the usual properties of TiC synthesized by this route, the finer sizes of the milled products are expected to yield improved properties than the TiC produced through conventional routes.5)
pling to ensure a constant BPR maintained over the entire duration of milling. A portion of the milled samples were heated at 10°C/min to 1000°C under an argon protective atmosphere in a tube furnace and held at this temperature isothermally for 15 min. Characterization of the samples was done by using SEM-EDX and the evolution of phases in the reaction products were identified by using XRD. Purification of samples were done by using HCl at different dilutions (1%–10%) with varying leaching time (10 h–30 h).

3. Results and Discussion

3.1. Powder Morphology Analysis with SEM

The particles of raw materials after normal mixing had irregular shapes with sharp angular edges as shown in Fig. 1(A). The powder particles became finer after a short milling time (10 h) as shown in Fig. 1(B) due to the milling action. Longer milling time (40 h), however, led to form large agglomerates due to continuous deformation which created new surfaces on particles with higher energy and enabled the particles to weld together as shown in Fig. 1(C). There was no considerable change in the shape and size of the particles noticed even after the heat treatment indicating the absence of de-agglomeration at high temperature (Figs. 1(D) and 1(E)).

3.2. X-ray Diffraction Analysis Results

During the early stages of milling, C atoms diffuse along the grain boundaries, and at the same time some C atoms may react with Ti atoms at the contact points along the grain boundaries. The XRD analysis of the samples milled for different durations are shown in Fig. 2.

The TiC formation was expected to be initiated at the early stage of milling because of the presence of Ti in its elemental state. In the present set of experiments, its presence is detected at all the stages of milling indicating the gradual diffusion of C atoms into the Ti lattice. The XRD patterns of as-milled mixtures milled over different durations (10 h, 20 h, 30 h, and 40 h) indicate the onset of TiC formation even with 10 h milling due to the chemical reaction and phase transformation taking place through mechanochemical processes, whereas the line broadening in Fig. 2 is observed due to refinement in particle size as well as stress accumulated in the particles due to the ball milling.

The Fe–Ti–Al–C is a complex system due to several factors, such as formation of various phases at different temperatures and the activities of the elements. Therefore, for the Fe–Ti–Al–C system, major possible reactions between Ti–C, Fe–Ti, and Fe–C are considered as follows:

\[ \text{Ti} + \text{C} \rightarrow \text{TiC}, \quad G^\circ_{298} = 180.296 \text{kJ/mol} \] .......................... (4)

\[ \text{Fe–Ti} + \text{C} \rightarrow \text{TiC} + \text{Fe}, \quad G^\circ_{298} = -186.606 + 0.0132T \quad (\text{kJ/mol}) \] ........................................ (5)

\[ \text{Ti} + 2\text{Fe} \rightarrow \text{Fe}_2\text{Ti}, \quad G^\circ_{298} = -53.3 + 0.0537T \quad (\text{kJ/mol}) \] (6)

\[ \text{Fe} + 3\text{C} \rightarrow \text{Fe}_3\text{C}, \quad G^\circ_{298} = 25.92 - 0.023T \quad (\text{kJ/mol}) \] ........................................ (7)

The proposed reaction principle based on these equations is as follows: first, allotropic change Fe\(_\alpha\)→Fe\(_\gamma\) occurs at 765.6°C; second, the compound Fe\(_2\)Ti forms at 1078.4°C because of the eutectic reaction between Ti and Fe; third, reaction between C with melted Fe\(_2\)Ti causes the formation of TiC. At the same time, Al from Fe–Ti reacts with melted Fe\(_2\)Ti and these reactions emit high exothermic heat which further accelerates the reaction between Ti and C to form thermodynamically stable TiC at 1138.2°C; finally, owing to...
the reaction between remnant C and Fe at 1146.4°C, Fe₃C is formed. After mechanical activation at ambient temperature, the synthesis reaction temperature is expected to be lower than those used in the conventional carbothermic reduction. The lowering of synthesis reaction temperature is due to the enhanced reactivity of the reactants from mechanical activation. After ball milling of a Fe–Ti and graphite mixture at room temperature, the powder was undergone a subsequent heat treatment (1000°C for 15 min) to facilitate the formation of TiC in the milled mixture. In all the XRD traces, the obvious presence of TiC phase is noticed as shown in Fig. 3.

Figure 3 shows sharper peaks compared to those with the as-milled mixtures as the stresses are relieved due to heating and also the particle size becomes bigger. Presence of Fe peak in Fig. 3 indicated unreacted Fe even with 40 h milling time. The sharp peaks of TiC formed after 10 h and 20 h milling refer to the higher activation energy of the reactants which lead to produce TiC and growth of crystallites. Fe and Fe₃C phases have presented very weak peaks at 10 h and 20 h whereas 30 h and 40 h milling durations show that the Fe peak decreases and the Fe₃C peaks increases even though no Fe₂C peak is observed. It can thus be concluded that Fe₂C in the as-milled mixtures were unstable and lost carbon to be converted to stable Fe₃C during heat treatment.

There is observable peak broadening in the XRD traces with progressive milling as shown in Fig. 3. The line broadening is caused by the reduction in crystallite size of the samples, the presence of the internal strain and local correlated disorder. This is due to large number of dislocations resulting from heavy deformation caused by high energy mechanical milling. Therefore, average crystallite size for TiC decreases with increase in milling durations at room temperature and after heat treatment of the as-milled samples at 1000°C for 15 min as shown in Fig. 4. The average crystallite size of TiC is estimated from the XRD traces in Figs. 2 and 3 by using the Scherrer equation (\(D = \frac{k \lambda}{B \cos \theta}\)), where \(D\) is the average crystallite size, \(k\) is the Cu Kα wave length, \(B\) is the diffraction peak width at half-maximum intensity and \(\theta\) is the Bragg diffraction angle. The crystallite size of TiC after milling for 10 h, 20 h, 30 h, and 40 h are 10.4 nm, 8.0 nm, 7.4 nm, and 6.0 nm, respectively. The crystallite size of TiC after milling for 10 h, 20 h, 30 h, and 40 h and subsequently heat treated at 1000°C are 23.3 nm, 17.9 nm, 17.3 nm, and 12.9 nm, respectively, as shown in Fig. 4.

The crystallite size of the synthesized phases is reduced by deformation process to saturation value with long milling time. The sample with 10 h milling time had high activation energy of the reactants with minimum contaminations and amorphous phases at room temperature which made easier phase transformations and crystallite growth of TiC at 1000°C.

### 3.3. Purification of TiC

#### 3.3.1. Effect of Concentration of HCl and Leaching Time

In this study, the production of TiC powders from (Fe–Ti+C) powder involves ball milling and heat treatment coupled with HCl leaching process. Generally, the leaching time, acid concentration, temperature, and particle size affect the dissolution of the iron. Leaching was performed at room temperature with different concentrations (1%, 3%, 5%, and 10%) of HCl for different leaching time starting from 10 h to 30 h. The dissolution rate of iron at various concentrations of HCl depends on the temperature of the reaction system; the leaching was performed at room temperature which led to using relatively high concentration of HCl. By comparing XRD patterns of the solid before and after leaching, the Fe and Fe₂Ti were found to be removed completely with HCl as shown in Fig. 5.

The sharp peaks of TiC and Fe₃C are observed while using 10% and 5%HCl for 10 h, 20 h, and 30 h as shown in Fig. 6 which indicate that the 10% and 5%HCl with a leaching time of 10 h can dissolve Fe and Fe₂Ti even at room temperature due to the chemical dissolution of iron by acid. Fine particles size of (TiC, Fe₂Ti, Fe₃C, Fe) mixture increase the dissolution of iron due to the large surface area. Therefore, it is preferable to do leaching by lower HCl concentration (1%, and 3%HCl) to reduce the cost of leaching process.
Lower concentration of HCl (1% and 3%) can also dissolve Fe and Fe$_2$Ti at room temperature due to the large surface area of the mixture (containing TiC, Fe$_3$C, Fe$_2$Ti, and Fe). Only peaks of TiC and Fe$_3$C, however, are observed by using 1% and 3%HCl for 10 h as shown in Fig. 7.

4. Conclusions

The novel use of Fe–Ti in the synthesis of TiC has been successfully explored. With the aid of mechanical activation at ambient temperature, the synthesis reaction of the mechanochemical process is occurring at a temperature far lower than those used in the conventional carbothermic reduction. The lowering of synthesis reaction temperature is due to the enhanced activation energy of the reactants achieved from mechanical activation even after 10 h milling which leads to the onset of formation and growth of crystallites of TiC at lower temperature (1000°C). Along with TiC, carbides of iron also form simultaneously. At the ambient temperature, only Fe$_2$C forms which gets converted to Fe$_3$C during heat treatment at 1000°C. The crystallite size of TiC decreases with increasing milling time but increases with increase in heat treatment temperatures.

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