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**RESEARCH NOTES**

# Synthesis of TiC Powder by Mechanical Alloying of Titanium and Asphalt*

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**Abstract** TiC powder was synthesized by mechanical alloying of titanium and asphalt in this paper. Deoiled asphalt as a carbon source not only provided element C in the fabrication of TiC but also cracked itself by the mechanical alloying process. The results of X-ray diffraction demonstrated the synthesis of cubic TiC. Gas phase chromatography showed that the discharged gas was composed of low molecular weight hydrocarbons, including $H_2$, $CH_4$ and $C_2H_6$. The formation mechanism of titanium carbide by mechanical alloying, and the thermodynamic and kinetics were discussed. These results showed that mechanical alloying is a promising method to prepare TiC and to crack asphalt with some light fraction byproducts.
**Keywords** asphalt, titanium carbide, mechanical alloying

## 1 INTRODUCTION

Heavy oil resources become increasingly important with increasing demand of global economy. Various techniques have been developed for the conversion of heavy oil to useful products, by catalytic cracking, coking, visbreaking, hydrotreatding, hydrocracking and solvent deasphalting *etc*.[1,2]. Also, many byproducts such as petroleum coke and deoiled asphalt are accumulated in huge stock. In fact, the main element in asphalt is carbon[3]. Therefore, asphalt can be utilized as a carbon source for preparing some other value added materials, *e.g*., carbide.

Mechanical alloying (MA) is a powerful solid-state powder processing technique involving repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill at room temperature[4—7]. By an MA process, blended materials could be alloyed at the atomic level. Recently, significant attention has been focused on the so-called reactive milling, in which solid-state reaction could occur at room temperature by milling blended powders to get alloy powders[8]. For example, MA has been successfully applied in synthesizing TiC powders by milling the blends of titanium/graphite[9], titanium/petroleum coke[10], titanium/hexane[11] or titanium/fullerene[12].

In this paper, asphalt and titanium powders were mixed and ball-milled, TiC compound was synthesized by solid state reaction. Besides, byproducts including gaseous $H_2$, $CH_4$ and $C_2H_6$ were also obtained, which are considered to be important energy sources in the future. The mechanism of this synthesis was discussed.

## 2 EXPERIMENTAL

### 2.1 Raw materials

Elemental Ti (＞99.9 %, ＜75μm), graphite (＞99 %, ＜75μm) and asphalt powder (＜250μm) were used. The deoiled asphalt used in this experiment was obtained by vacuum residue from butane deasphalting. The composition of the asphalt was measured with elemental analyzer (model EA1108, Carlo Erba, Milan, Italy) and listed in Table 1.

**Table 1 Property of the asphalt in the present work**

| C, % (by mass) | H, % (by mass) | S, N and O, % (by mass) | Density at 20℃, $g\cdot cm^{-3}$ | Softening point, ℃ |
|---|---|---|---|---|
| 86.73 | 9.80 | ＜3.47 | 1.05 | 125 |

### 2.2 Process of mechanical alloying

Mixed powders of Ti and C material were mechanically alloyed in a QM-ISP planetary ball mill at ambient temperature. The powders (5g) were mixed and sealed in a stainless steel vial (500ml capacity) under an argon atmosphere. The mass ratio of ball to powders was 50∶1. Two kinds of hardened steel balls of $\phi$20mm and $\phi$6mm diameter were selected. The rotational speed was $200r\cdot min^{-1}$.

Ti and graphite mixture powders were milled in a Ti/C atomic ratio of 50∶50. According to the composition of the deoiled asphalt, different atomic ratios of titanium to carbon in Ti-asphalt powders were selected as shown in Table 2.

**Table 2 Atomic ratio of titanium to carbon**

| Samples | Composition (atomic ratio) | | Milling time, |
|---|---|---|---|
| | Ti | C | h |
| Ti-asphalt (Ⅱ) | 33.3 | 66.7 | 45 |
| Ti-asphalt (Ⅰ) | 50 | 50 | 45 |
| Ti-graphite | 50 | 50 | 30 |

### 2.3 Instrumentation

The samples milled in different conditions were

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taken from the vial and then analyzed by X-ray diffraction (XRD) using a Rigaku DMAX-RB diffractometer with Cu $K_{\alpha}$ radiation. The morphology of the powders was observed by using a scanning electron microscope (SEM, Oxfords-360). The gas yielded during milling was collected and analyzed by Aglient-6890 gas phase chromatography.

## 3 RESULTS AND DISCUSSION

### 3.1 Effects of mechanical alloying in different conditions

It has been reported[13,14] that Ti-graphite powder can transform into TiC compound completely. After milling of the Ti-graphite powders for 30 h in this work, Ti was all transformed into TiC as observed from XRD in Fig.1. The time needed for synthesis of TiC by milling the Ti-asphalt ( Ⅰ ) powder was 45h, and then the yield was near 100%. TiC can not be found with the increasing of the C to Ti ratio, as can be seen in Fig.1, whereas only Ti peaks appeared in the XRD pattern of the Ti-asphalt (Ⅱ) powder milled for 45h.

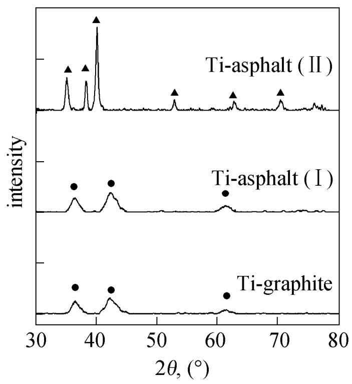



**Figure 1 XRD patterns of different powders after milling**
▲Ti; ● TiC

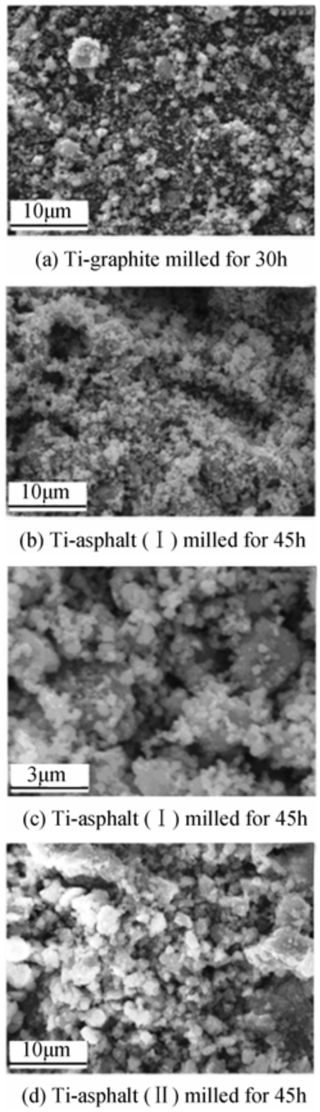
The size and morphology of the powders after milling were examined by SEM, as shown in Fig.2. It can be seen that for the Ti-graphite system, the obtained TiC powders had an average size of about 1μm. The grain size of the TiC powder formed by milling of Ti-asphalt ( Ⅰ ) for 45h was about 300nm, much smaller than that in Fig.2(a). For the Ti-asphalt (Ⅱ) system after 45h of milling, one can see lots of big block in heterogeneous sizes, which were unreacted titanium and asphalt powders in Fig.2(d).

According to the results of the gas phase chromatography, some hydrocarbons such as $H_2$, $CH_4$ and $C_2H_6$ were emitted (Fig.3). The volume percentage of $H_2$, $CH_4$ and $C_2H_6$ was 2.54%, 83.78% and 11.94%, respectively.

### 3.2 Mechanism of MA solid reaction

The mechanism of this process can be described in the view of thermodynamics. In this exothermic reaction, the formation heat ($\Delta_f H_{298K}=-184 kJ\cdot mol^{-1}$) is a negative value, which decreased the free energy and hence benefits the formation of TiC.

The element H of deoiled asphalt was mostly released in the form of hydrogen, methane and ethane gas. The XRD pattern showed no titanium hydride peaks. These information indicated Ti have higher selectivity of bonding with element C than element H. This phenomenon can also be explained in aspect of thermodynamics by the fact that $\Delta_f G_{298K}$ (Gibbs free energy of formation) of TiC is less than that of $TiH_2$ ($\Delta_f G_{298K,TiC}=-180.844 kJ\cdot mol^{-1}$, $\Delta_f G_{298K,TiH_2}=-105.073 kJ\cdot mol^{-1}$).




(a) Ti-graphite milled for 30h
(b) Ti-asphalt ( Ⅰ ) milled for 45h
(c) Ti-asphalt ( Ⅰ ) milled for 45h
(d) Ti-asphalt (Ⅱ) milled for 45h

**Figure 2 SEM micrographs of powders**

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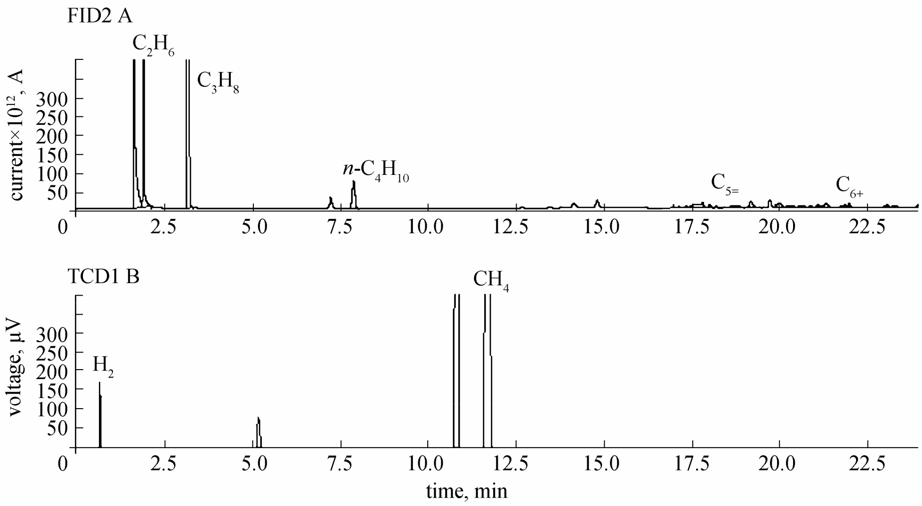


**Figure 3 GC-FID/TCD chromatogram of emitted gas at 45h from Ti-asphalt (Ⅰ) mixture**


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