Synthesis and structural evolution of vanadium carbide in nano scale during mechanical alloying

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Abstract In this study, nano crystalline vanadium carbide was synthesized by mechanical alloying method. V2O5, C and Mg powders were placed in a planetary ball mill and sampled after different milling times. XRD and FESEM were used for characterization of synthesized powder. Studies showed that crystalline V8C7 has been synthesized by 24 h milling and subsequently heat treatment at 800 °C. It was concluded that the V8C7 crystallites were nano sized and the lattice parameter deviated slightly from the standard size. Furthermore, milling led to increase in strain and decrease of vanadium carbide particle size.

1. Introduction

The transition metal carbides have very high melting points, hardness and high temperature strength. These materials also exhibit good electrical and thermal conductivities. Among them vanadium carbide is the most attractive because of its many excellent physical and mechanical properties such as high hardness, excellent wear resistance, good corrosion resistance, excellent high temperature strength, high chemical and thermal stability even at high temperatures. It is commercially used in tool bits and cutting tools (Mahajan et al., 2013; Kurlov et al., 2013; Ye et al., 2009; Chen et al., 2011; Oelerich et al., 2001).

Presently, various methods for synthesizing vanadium carbide powders have been investigated including direct element reaction (Schwarzkopf and Kieffer, 1953), mechanical alloying (Dai et al., 2012), temperature programmed reaction (Lin et al., 2012), gas reduction-carburization (Mahajan et al., 2012; Zheng et al., 2012). Mechanical alloying (MA) as production process in cemented carbides has attracted many interests due to its capability of producing nano-crystalline powders prior to sintering (Dai et al., 2012; Zheng et al., 2012). This method has a number of potential advantages. MA process is simple, cheap and can be performed at ambient temperature. Mechanical alloying (MA) is a popular method to fabricate materials with...
novel structures and/or properties (Suryanarayana, 2001; Hoseinpur et al., 2013; El-Eskandarany, 2001).

Although some research were done for synthesizing vanadium carbide by mechanical alloying, but the effect of microwave heating after milling on the properties of synthesized materials was not investigated. So, this paper focused on synthesis and structure evolution during synthesis of $V_8C_7$ nano powder by MA method. Also the effect of microwave heating after milling on particle size, lattice parameter and phase formation of vanadium carbide was investigated.

2. Experimental

2.1. Materials and treatments

The starting materials were commercially available powders of $V_2O_5$ (purity of 99.9% and mean particle size of 200 µm), magnesium (purity of 97% and mean particle size of 100 µm) and amorphous graphite (purity of 99.8% and mean particle size of 50 µm). All the input materials with stoichiometric ratio were mixed according to the following reaction:

$$V_2O_5 + 5Mg + 2xC = 2VC_x + 5MgO \quad (1)$$

A SPEX ball mill with stainless vials (volume 250 ml) and balls (diameter 20 mm) was used for the mechanical milling. In order to protect the materials from oxidation, the vial was sealed with high-purity argon with a pressure of about 1 MPa. The ball to powder weight ratio was 20:1. Milling was carried out at a rotation speed of 250 rpm for 1, 3, 6, 12, 18 and 24 h.

Since vanadium carbide is chemically stable at room temperature and cannot be easily attacked even by strong acids, to remove the by-product (MgO), the as-milled powders were treated with 5% acetic acid solution. To complete phase formation, microwave heating was performed for 24 h milled samples.

The samples were placed into a microwave heater with power of 900 W and frequency of 2.45 GHz. A SiC crucible was used as a susceptor due to its efficient absorbance of microwave energy (Oghbaei and Mirzaee, 2010; Razavi et al., 2009).

2.2. Characterization

The synthesized powders were characterized by X-ray diffraction (Bruker D8) with the voltage and current of 40 kV and 30 mA, respectively, and Cu Kα radiation ($\lambda = 1.54\text{Å}$). The crystallite size was evaluated through the Williamson–Hull method (Eq. (2)) Razavi et al., 2009; Razavi et al., 2012 and the lattice parameter was also obtained using the Nelson–Riley method (Eq. (3)) Razavi et al., 2009; Razavi et al., 2012; Tsai et al., 1989.

$$b \cos \theta = \frac{0.9\lambda}{d} + 2\eta\sin \theta \quad (2)$$

![Figure 1](image)

**Figure 1** X-ray diffraction patterns of the (a) VC–MgO system which were milled in different times and (b) 24 h milled powders after microwave heating and leaching ($V_4C_3$ (●), MgO (▼), Mg (+), $V_2O_5$ (*), $V_8C_7$ (*)).
The structural characterization of the samples was carried out by Field Emission Scanning Electron microscopy (FESEM) Hitachi S-4160. Gold coating was given for improving conductivity for the samples analyzed.

### 3. Results and discussion

#### 3.1. VC–MgO binary system

X-ray diffraction patterns of the powders containing V$_2$O$_5$, Mg and C milled for different times are shown in Fig. 1a. The products derived were MgO (PCPDF No. #004-0829) and V$_4$C$_3$ (PCPDF No. 00-001-1159).

In the time of zero, only the V$_2$O$_5$ and Mg peaks are observed. As it is clear in Fig. 1a, the powders milled for 6 h transformed to V$_4$C$_3$ and MgO without any other phases. Further milling has no influence on the type of the existing phases. For more than 6 h, the peaks broadened slightly, which is the result of the fineness of the crystallites (Razavi et al., 2012). Nowadays, two kinds of mechanisms for MA have been widely accepted (Razavi et al., 2012):

I. Gradual elemental diffusion under the action of colliding balls.

II. Sudden formation of products in a short period of milling time and consequently occurrence of mechanically alloyed self-sustaining reaction (MSR).

Vanadium carbide formation from V and C raw materials can be explained with second mechanism (Dai et al., 2012).

### Table 1

The mean size of the crystallites and the strain caused by milling in VC–MgO system ($\eta$: strain, $d$: grain size, $R^2$: regression coefficient).

<table>
<thead>
<tr>
<th>Milling time (h)-temperature (°C)</th>
<th>$b\cos \theta = \frac{0.92}{2} + 2\eta \sin \theta$</th>
<th>$d_{(\text{max})}$</th>
<th>$\eta_{(\text{c})}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-0</td>
<td>0.0024</td>
<td>51.33</td>
<td>0.24</td>
<td>0.994</td>
</tr>
<tr>
<td>12-0</td>
<td>0.0049</td>
<td>40.76</td>
<td>0.49</td>
<td>0.969</td>
</tr>
<tr>
<td>18-0</td>
<td>0.0061</td>
<td>26.15</td>
<td>0.61</td>
<td>0.986</td>
</tr>
<tr>
<td>24-0</td>
<td>0.0069</td>
<td>21.32</td>
<td>0.69</td>
<td>0.981</td>
</tr>
<tr>
<td>24-800</td>
<td>0.0036</td>
<td>33.8</td>
<td>0.36</td>
<td>0.965</td>
</tr>
</tbody>
</table>

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I. Gradual elemental diffusion under the action of colliding balls.

II. Sudden formation of products in a short period of milling time and consequently occurrence of mechanically alloyed self-sustaining reaction (MSR).

Vanadium carbide formation from V and C raw materials can be explained with second mechanism (Dai et al., 2012).
The as-milled powder after 24 h milling was leached with an acetic acid solution. To complete the phase formation, microwave heating was performed for 24 h milled samples. The temperature of the samples was held at 800 °C during 15 min of microwave heating.

The results showed that the diffraction peaks of MgO disappeared and a powder consisting of single phase V₈C₇ was obtained (Fig. 1b).

Okamoto (2010) investigated the diagram of V–C system for the transformation of the fcc-(VCₓ) phase to V₆C₅ and V₈C₇ phases. V₄C₃ is not stable at room temperature and if enough thermal activation is provided, the additional carbon in the mixture will enter into the carbide lattice interstitial sites and V₄C₇ would be formed. Effective microwave energy leads to easier formation of V₄C₇ at the existing stoichiometry.

The mean size of the crystallites and the strain percentages of the samples before heat treatment are illustrated in Table 1. The Williamson–Hall equation was used \( b \cos \theta = \frac{0.9 \lambda}{d + 2 \eta \sin \theta} \) where \( b \) is the peak full width at half-maximum (FWHM), \( \theta \) the diffraction angle, \( \lambda \) the wavelength of the X-ray, \( d \) is so called crystallite dimension, and \( \eta \) is an approximate upper limit of the lattice distortion. Fig. 2a shows Williamson–Hall diagram of this system after 6, 8, 12 and 24 h milling. As it is clear in Fig. 3, by increasing the milling time, the milling efficiency decreases and the refinement and the reversion of grains tend to get their dynamic balance, so the

![Figure 3](image.png)

*Figure 3* Variation of crystallite size and strain in synthesized powders vs. milling time.

![Figure 4](image.png)

*Figure 4* Determination of VCₓ lattice parameter using Nelson–Riley method.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Heat treatment temperature(°C)</th>
<th>( a₀ )(nm)</th>
<th>Space group</th>
<th>( a₀–a₁ )(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milling time (h)</td>
<td>24</td>
<td>0.4107</td>
<td>Fm-3 m</td>
<td>0.0053</td>
</tr>
<tr>
<td>24</td>
<td>800</td>
<td>0.8307</td>
<td>P4132</td>
<td>0.0027</td>
</tr>
</tbody>
</table>

*Table 2* Calculation of produced VCₓ lattice parameter in VC–MgO binary system.
refining rate of crystallite size is reduced and the powder crystallite size reaches its limit (21.32 nm).

In order to determine the crystallite size after heat treatment Williamson–Hall method was used again (Fig. 2b). These quantities are presented in Table 1. It can be seen that crystallite size after microwave heating does not grow up considerably and remains at nanometer range.

The lattice parameter of $V_4C_3$ and $V_8C_7$ can be calculated in accordance with the Nelson–Riley equation. By extrapolation of the curves in Fig. 4 and determination of the best fitted curve intersect at $X = 0$ abscissa, the lattice parameter of $V_4C_3$ and $V_8C_7$ can be derived (Razavi et al., 2012).

In Table 2 $a_0$ is the calculated and $a_{st}$ is the standard lattice parameter of $V_4C_3$ and $V_8C_7$. In accordance to files

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**Figure 5** FESEM micrograph of powders milled for (a) 0 h, (b) 3 h, (c) 6 h, (d) 12 h, (e) 18 h, (f) 24 h and the particle size of VC$_x$, (g) after 24 h milling (h) after 24 h milling and subsequent microwave heating.
00-019-1394 and 00-001-1159 of the international center for diffraction data (JCPDS-ICDD 2000), the lattice parameters of $V_3C_7$ and $V_3C_3$ are 0.8334 and 0.4160 nm respectively. The calculations are presented in Table 2.

Performing heat treatment increases the lattice parameter which implies strain relieving. Vanadium and carbon form a cubic monocarbide $VC_x$ of B1 (NaCl) structure. A feature peculiar to the structure of the strongly non-stoichiometric $VC_x$ is the intrusion of carbon atoms in the octahedral interstices of the metallic sites. Significantly, the carbon atoms may occupy only a fraction of the interstitial sites, and the rest are filled with structural vacancies (Porter et al., 1992). The ratio of $C:F$ is 0.66–0.88 at ambient temperature (Dai et al., 2012). Thus, the deviation of the lattice parameter can be caused by non-stoichiometric ratio of the synthesized carbide (Razavi et al., 2012).

3.2. Microstructural characterization

Fig. 5 shows FESEM micrographs of nano powders at different milling times. As Fig. 5a illustrates, the as-received particles exhibit flake shape with relatively broad size distribution. After 3 h milling, the initial particles were deformed and a change from spherical to irregular shape was noticed (Fig. 5b). When longer milling time was applied the particles were flattened and spherical like particles were formed (Figs. 5c and d). Micro-welding between the particles was also observed. The welded areas were more noticeable after 18 h milling (Fig. 5e). At milling time of 24 h, the fragmentation of the flattened particles was detected although the shape of particles was still spherical-like (Fig. 5f).

The particle size powder of $V_3C_7$ after 24 h MA was investigated at two conditions: before and after heat treatment at 800 °C for 15 min. Fig. 5 shows that the particle size after heat treatment is slightly greater than its value before (60 versus 42 nm). Also it confirms the results of Williamson–Hall method.

4. Conclusions

The most important findings in this research can be summarized as follows:

A. $V_3C_7$ nano powder was successfully obtained from $V_2O_5$, Mg and C powders via combined mechanochemical process and subsequent microwave heating.

B. The particle size of $V_3C_7$ nanoparticles was about 42 nm before and 60 nm after microwave heating. These values confirm to some extent the crystallite size obtained from Williamson–Hall equation.

References


