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Mechanochemical Carboaluminothermic Reduction of V_2O_5 to Produce VC-Al_2O_3 Nanocomposite

Mohsen Hossein-Zadeh[a], Fatemeh Tebyani[a], Javad Yazdani Cherati[a], Omid Mirzaee[a]*

[a]*Department of Materials Engineering, Semnan University, Semnan, Iran*

*Corresponding author: o_mirzaee@.semnan.ac.ir, omidmirzaee@yahoo.com

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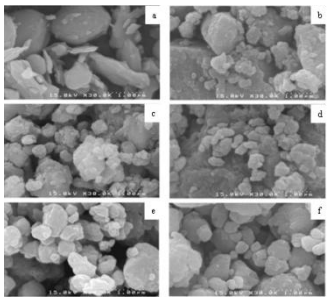
Graphical abstract



Abstract

The aim of this investigation is to produce VC–Al_2O_3 nanocomposite by reducing V_2O_5 with Aluminum and black carbon powders via mechanochemical process. The effect of milling time on this process was investigated. Milling process was done powder mixture at a rotation speed of 250 rpm for different times. Results showed that VC_x has been synthesized after 1 hour of milling. The characterization of phase formation, crystallite size, strain percentage and lattice parameter was done by XRD analysis. To study the morphological evolution and determination of particle size of nanocomposite powders, Field Emission Scanning Electron Microscope (FESEM) was used. The crystallite size and lattice strain were determined by Williamson-Hall method. XRD study showed that for 6 h milling, the width of V_4C_3 peaks increased while the crystallite size of these phases decreased to about 27nm. In order to formVC–Al_2O_3 nanocomposite, the mixture was heat treated with the aid of microwave oven. The composite revealed good microwave absorption and heated up to 1150°C.

Keywords: Mechanochemical process; vanadium carbide; heat treatment, X-ray diffraction

1.0 INTRODUCTION

Metal carbides are the leading advanced engineering ceramics used in metal working, electrical and electronic, automotive, and refractory industries. This is due to their high temperature strength retention, excellent oxidation resistance, low thermal expansion coefficient, high wear resistance, high melting point and light weight. Among them VC is one of 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 [1-4]. It is an extremely hard refractory ceramic material. It is commercially used in tool bits and cutting tools [5]. Presently, various methods for synthesizing vanadium carbide powders have been investigated, including direct element reaction [6-9], mechanical alloying [10], temperature programmed reaction [9], gas reduction-carburization [5, 9] aluminothermic reduction of vanadium oxide and the carburization of vanadium oxide with an organic reagent such as cyanamide [5]. 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 [1]. 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 [11-13].

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. Therefore, they have been comprehensively studied by many investigators, working on extractive metallurgy, materials synthesis and production of nano-crystalline and amorphous materials [14].

This paper focused on synthesis and structure evolution during synthesis of V_8C_7 nano powder by MA method. The effect of microwave heating after milling on lattice parameter of vanadium carbide on final product was also investigated.

2.0 EXPERIMENTAL PROCEDURE

2.1 Material and Treatments

The starting materials were commercially available powders of V_2O_5 (purity of 99.9% and mean particle size of 200μm), aluminum (purity of 97 % and mean particle size of 80μm) and black carbon (purity of 99.8% mean particle size 50μm). All the

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

$$3V_2O_5 + 10Al + 6C \rightarrow 6VC + 5Al_2O_3 \quad (1)$$

A SPEX ball mill with stainless vials (volume 250 ml) and balls (diameter 20mm) 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 1MPa. The ball to powder weight ratio was 20:1. Milling was carried out at a rotation speed of 250 rpm for 0.5, 1, 1.5, 3 and 6 h. To complete phase formation, microwave heating was performed for 6 h milled sample. The sample was heated into a microwave heater up to 1150°C with the power of 850W and the frequency of 2.4 GHz. A SiC crucible was used as a susceptor due to its efficient absorbance of microwave energy [13]. The powders were characterized by X-ray diffraction (Bruker D8 model) with the voltage and current of 40 kV and 30 mA, respectively, and Cu Kα radiation (λ = 1.54A°). The crystallite size was evaluated through Williamson–Hall method as shown in equation 2 [12] and the lattice parameter was also obtained using Nelson–Riley method as shown in equation 3 [12, 15].

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

$$F(\theta) = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \quad (3)$$

The microstructural examination of the samples was carried out by Field Emission Scanning Electron microscopy (FESEM) Hitachi S-4160 model. Gold coating was given for improving conductivity for the samples analyzed.

3.0 RESULTS AND DISCUSSION

3.1 VC–Al_2O_3 Binary System

X-ray diffraction patterns of the powders containing V2O5, Al and C which have been milled for different times are shown in Figure 1. The products derived were Al2O3 (PCPDF no. 00-001-1243) and V4C3 (PCPDF no 00-001-1159).

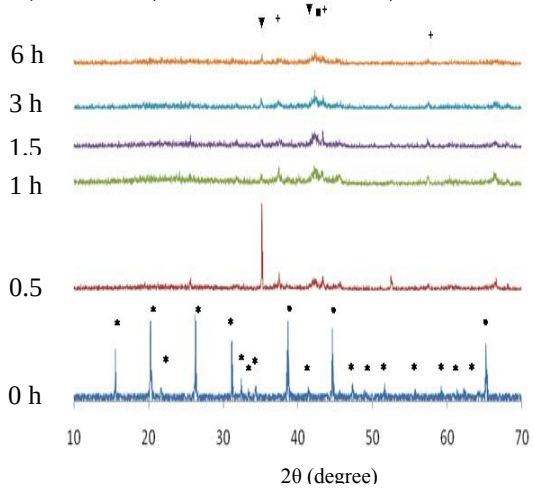


Figure 1 X-ray diffraction patterns of the VC–Al_2O_3 system different times (V_4C_3 (+), Al_2O_3 (▼), Al (●), V_2O_5 (*), V (■))

In the time of zero, only the V_2O_5 and Al peaks are observed. There are no peaks from C because the carbon black used in the experiment was amorphous. At the time of 1 h the peaks of V_4C_3 have been appeared. Milling, even for long times, did not have any influence on the type of the existing phases and the only observable phases are V_4C_3 and Al_2O_3. Also milling for 6 h, only the peaks broadened slightly and diminished in intensity, which are the results of the fineness of the crystallites [7]. This observation is anticipated because that V_2O_5 is a very stable phase and formation of VC from this phase needs a large amount of energy that cannot be supplied from milling process. Nowadays, two kinds of mechanisms for MA have been widely accepted [15]:

I. Gradual elemental diffusion under the action of colliding balls
II. Suddenly formation of products in a short period of milling time and consequently occurrence of mechanically alloyed self-sustaining reaction (MSR).

VC formation from V and C raw materials can be explained with second mechanism [16]. To complete the phase formation, microwave heating was performed for 10 minutes on powders. After that V_4C_3 weak peaks were completely replaced by V_8C_7, Al_2O_3 and $AlCV_2$ (Figure 2).

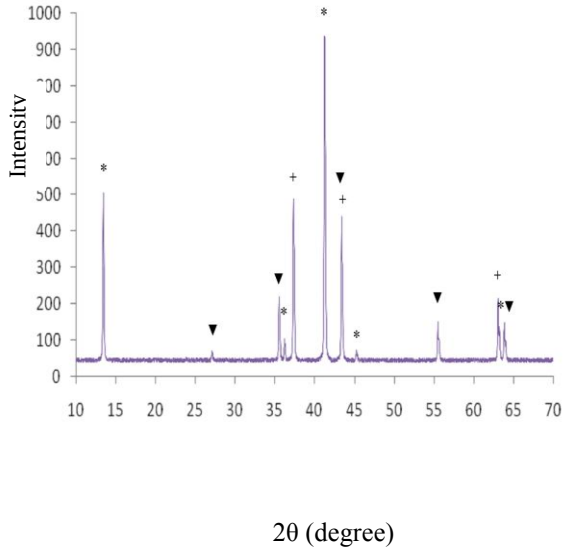


Fig.ure 2 X-ray diffraction patterns of the VC–Al_2O_3 system that was heated in microwave furnace after milling 6h (V_8C_7 (+), Al_2O_3 (▼), $AlCV_2$ (*))

The crystalline size and strain percentage of VC_x were derived from Williamson–Hall equation ($b\cos\theta = 0.9\lambda/d + 2\eta\mathrm{Sin}\theta$) where b is the peak full width at half-maximum (FWHM), θ the diffraction angle, λ the wavelength of the X-ray, d is so called crystallite dimension, and η is an approximate upper limit of the lattice distortion. Figure 3 shows Williamson–Hall diagram of this system after 6 h milling.

The mean size of the crystallites and the strain percentage are illustrated in Table 1.

Table 1 The mean size of the particles and the strain caused by milling in VC– Al_2O_3 system (η: strain, d: grain size, R^2: regression coefficient)

Milling time (h)	$b\cos\theta = 0.9\lambda/d + 2\eta\sin\theta$		$d_{VC\ nm}$	$\eta_{VC\ \%}$	R^2
	η	$0.9\lambda/d$			
6	0.0036	0.005	27.72	0.36	0.899

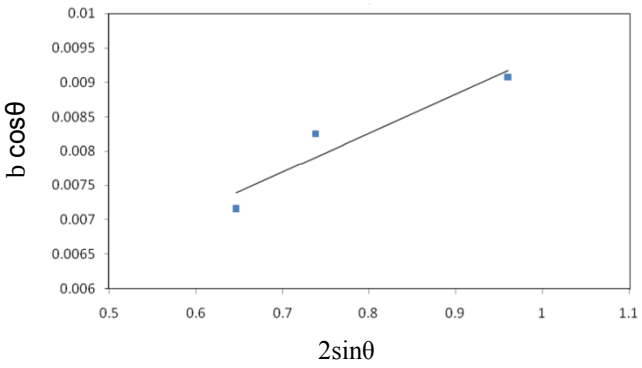


Figure 3 Williamson–Hall diagram of the VC–Al_2O_3 system

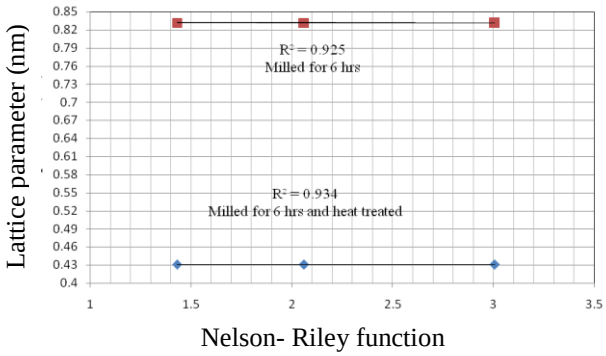


Figure 4 Determination of VC lattice parameter using Nelson–Riley method

The other effects of mechanical alloying are increasing of lattice parameter [15]. The lattice parameter of VC can be calculated in accordance with Nelson–Riley equation. By extrapolation of the curves in Figure 4 and determination of the best fitted curve intersect at $X = 0$ abscissa, the lattice parameter of VC can be derived [15]. 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 00-019-1394 and 00-001-1159 of the international center for diffraction data (JCPDS-ICDD 2000), the lattice parameter of V_8C_7 and V_4C_3 are 0.8334 nm and 0.4165 nm respectively. The calculations are presented in Table 2.

Table 2 Calculation of produced VC lattice parameter in VC–Al_2O_3 binary system

Condition		a_o (nm)	Space group	$a_{ST} - a_0$ (nm)
Milling time(h)	Heat treatment temperature(°C)			
6	-	0.4132	Fm-3m	0.0033
6	1150	0.8320	P4132	0.0014

Performing heat treatment increases the lattice parameter, which implies strain relieving. In spite of the difference in space group and lattice parameter, V_4C_3 and V_8C_7 have the same atomic arrangement if the C vacancies are not taken into account.

Vanadium and carbon form a cubic monocarbide VCx 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 rests are filled with structural vacancies. Since the annealing temperature was not high enough [16], only the positions of the C vacancies changed in this system [16-18].

3.2 Microstructural Examination of Milled Powders

FESEM analyses were carried out to observe morphologies of the nano-VC_x powders. Figure 5 shows FESEM micrographs of nano- VC_x powders at different milling times. As Figure 5a illustrates, the as-received particles exhibit flake shape with relatively broad size distribution. After 0.5 h milling, the initial particles were deformed and a change from spherical to irregular shape was noticed (Figure 5b).

When longer milling time was applied, the particles were flattened and spherical like particles were formed. In the intermediate stage the powders get work hardened, the hardness and consequently the brittleness increases [14].Hence, fracture is the main process, and the powders become finer in size in comparison with those in the initial stage and some agglomerates are formed as shown in Figs. 5c and d. Micro-welding between the particles was also observed. The welded areas were more noticeable after 3 h milling (Figure 5e).

At milling time of 6 h, the fragmentation of the flattened particles was detected, although the shape of particles was still spherical -like (Figure 5f). By further milling time of 3 h,

steady-state equilibrium is obtained when a balance between cold welding and fracturing is achieved [14].

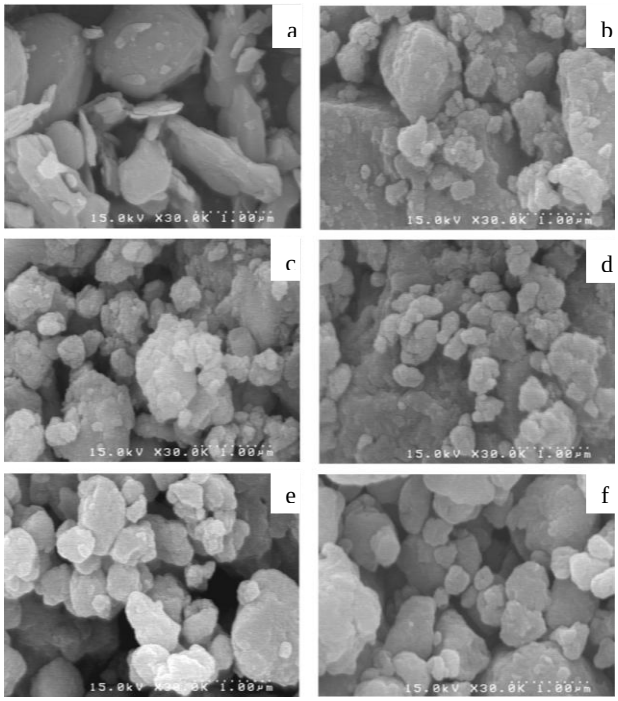


Figure 5 FESEM micrograph of powders milled for (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 1.5 h, (e) 3 h and (f) 6 h

After 6 h MA, powder heated in microwave. The grain size powder of V_8C_7 was investigated by FESEM.
Figure 6 shows that particles size after heat treatment. The size of grain from this image is almost 98.92 nm. Also it confirms the results of Williamhanson-Hall method.

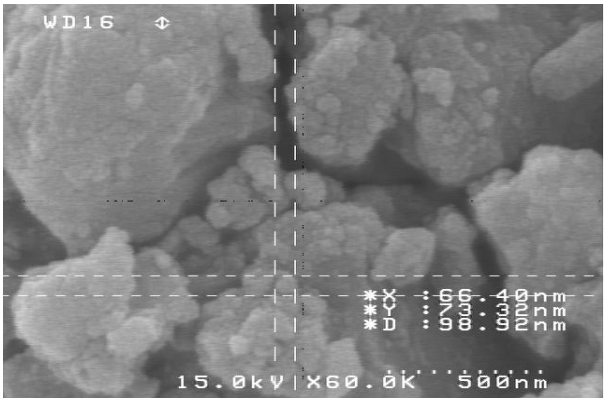


Figure 6 FESEM micrographs show the grain size of heated V_8C_7 powder after 6 h milling

■4.0 CONCLUSIONS

This study represents a comprehensive investigation on the preparation of vanadium carbide by Mechanochemical and subsequently heat treatment of VC–Al_2O_3 binary system. The mechanically solid state reacted powders have been characterized as a function of the milling time by means of XRD and FESEM. The findings can be summarized as followings:

- VC-Al_2O_3 nanocomposite was successfully obtained from V_2O_5, Al powders and carbon black via mechanical alloying in the milling times of above 6 h. V_4C_3 crystallite size was about 27 nanometer order.
- The morphologies of V_8C_7 nanoparticles were spherical and faceted structures were observed. The grain size of V_8C_7 is about 98.92 nm.

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