Powder Technology 217 (2012) 369–376

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Mechanochemical synthesis of nano TiC powder by mechanical milling of titanium and graphite powders

Mohammad Bagher Rahaei *, R. Yazdani rad, A. Kazemzadeh, T. Ebadzadeh

Materials and Energy Research Center (MERC), P. O. Box: 14155-4777, Tehran, Iran

ARTICLE INFO

Article history:
Received 24 February 2011
Received in revised form 7 October 2011
Accepted 24 October 2011
Available online 6 November 2011

Keywords:
TiC
Milling
Mechanochemical reaction
Nanopowder
Microstructure

ABSTRACT

In this research, the formation of TiC nanopowder was investigated by mechanochemical reaction of titanium and graphite starting materials during milling. The evolutions in temperature and pressure were evaluated using thermal-pressure sensor during milling. Phase transformation, grain size, strain, lattice parameter, introduction of Fe impurity, morphology of powders and particles size distribution during milling were examined using different analysis techniques including XRD, Rietveld refinement, ICP, SEM, TEM, Zeta sizer and BET. Nanocrystalline TiC was obtained by an abrupt increase in the temperature and pressure of the vial after a short milling time that confirmed mechanochemical mechanism by an exothermic reaction. Longer milling times resulted in decreasing of TiC particles size toward nanosize scale along with increasing of Fe impurity.

1. Introduction

Titanium carbide (TiC) is a material of commercial interest because it possesses a range of desirable properties such as high melting point, high modulus, great hardness, high chemical stability, etc. These properties have resulted in extensive use of TiC as a reinforcing phase in composites and superalloys [1–5].

TiC is also used as an anti-wear and anti-abrasion material in making cutting tools, grinding wheels, polishing paste, magnetic recording heads, crucible for smelting metals, etc. [1,6].

Normally, titanium carbide is produced by high-temperature processes such as the displacement reaction of titanium oxide and carbon, the direct chemical reaction of elemental Ti and C [7–11]. On the other hand, mechanical alloying (MA) is a rapidly developing technology capable of producing a variety of materials, such as compounds, metastable solid solutions, amorphous alloys, nanocrystalline materials, etc. [12]. Mechanical alloying is very simple and appears to be readily scalable: powders of new materials are produced by high-energy ball milling of starting ingredients [13]. Thermal explosion of the reactants can also occur during mechanical milling. This process is referred to as mechanically induced self-propagating reaction (MSR) [14].

Nanoparticles are essential building blocks to make many new materials with tailored optical, magnetic, mechanical, and electrical properties. Such particles are often anisotropic in shape and resemble disks, rods, or ellipsoids. Scientific interest in nanometer-sized particles focuses on size-dependent physical properties that include specific surface area, quantum confinement, and super paramagnetism [15].

Recently, researches have focused on the production of nanoscale or nanostructured TiC for improvement in hardness, mechanical strength and wear resistant of composite materials [1,16–18].

Chandra et al. [1] have reported that the size of the synthesized TiC powder depends on the size of starting materials and synthesized nanosize titanium carbide (diameter ~ 30–185 nm) by chemical reaction between titanium bearing precursor gel and nano carbon particles derived from soot at different temperatures in the range of 1300–1580 °C for 2 h under argon (Ar) atmosphere as a novel process.

Some researches have considered the influence of initial titanium and carbon sources on the formation of TiC during mechanical alloying, for example the formation of nanocrystalline TiC from titanium and different carbon sources (activated carbon, carbon fibers or carbon nanotubes) [16], different Ti/C ratios [18], and the synthesis of TiC powder from titanium and asphalt [19].

Although there are lots of researches focused on the production of nanostructured TiC using MA, the potential of this method for production of nanosized powder needs to be studied.

Characterization of both distribution and size of nanoparticles is important in the development of these materials and as a criterion to control the quality of the synthesis.

Rietveld's refinement method has also been becoming progressively popular for microstructural characterization of metallic and ceramic materials. It is a common practice to estimate average grain size and average strain values from the refined profile width parameters [20–23].

* Corresponding author. Tel.: +98 912 6035614; fax: +98 261 6201888.
E-mail address: m.b.rahaei@gmail.com (M.B. Rahaei).

0032-5910/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.powtec.2011.10.050

Therefore, in the present work, the formation of nanostructured TiC powder along with nanoscale particle size was investigated from titanium and graphite powders by MA process.

MSR mechanism during milling was evaluated by monitoring change of vial temperature and pressure during milling. The details of structural evolution of powder product during milling including grain size, root mean square (r.m.s) strain, lattice parameter and introduction of Fe impurity were investigated using XRD, Rietveld refinement, TEM and ICP analysis techniques.

Besides, characterization of powder product including particle size distribution and morphology was investigated using SEM, TEM, Zeta Sizer and BET analysis techniques.

2. Experimental procedure

2.1. Mechanical alloying process

In this investigation, Ti (99.5% purity) and graphite as a source of carbon (99% purity) powders were used as starting materials. Both Ti and C powders had an irregular shape with particle size between 5 and 50 μm (Fig. 1a and b).

A Retsch PM400 planetary mill equipped with a thermometer and pressure sensor, monitored by a wireless system inserted on the vial side, was utilized to measure the increase of vial temperature and pressure during milling process. The milling media consisted of four 20 mm diameter and three 14 mm balls confined in a 150 ml volume vial. The ball and vial materials were hardened steel. In all experimental operations, Ti and C powders in 1:1 molar ratio ($Ti_{50}C_{50}$) were mixed together and then milled for 1, 4, 8 and 16 h under Ar atmosphere. Stearic acid ($CH_3(CH_2)_{16}COOH$) in the quantity of 2 wt.% was utilized as Process-Control Agent (PCA) material to avoid sticking of the powders to the vial and balls.

In all MA runs, the ball-to-powder weight ratio (BPR) was 10:1. The vial rotation speed was approximately 300 rpm. To prevent sample oxidation, the powders were sealed in the vial under Ar atmosphere and a fresh sample was used for each ball milling run.

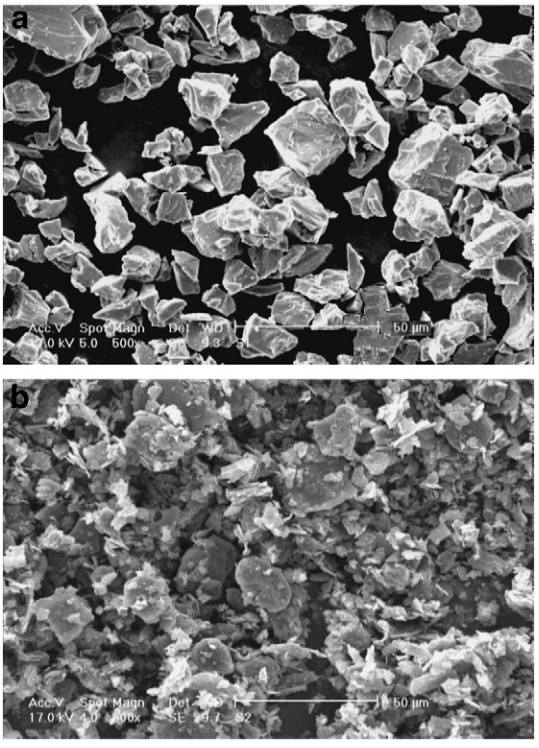

Fig. 1. SEM images of starting powder particles of a. Ti and b. Graphite.

2.2. Phase and structural evolutions using XRD and Rietveld analyses

2.2.1. XRD analysis

The structural evolution during milling was studied by X-ray diffractometer (XRD-Siemens D500) with Cu K_α radiation ($\lambda = 0.15406$ nm) operating at 30 kV and 25 mA. Two-theta was recorded in the range of 20° and 80° with a step size of 0.02 (counting time was 3 s per step at different polar tilting angles).

The lattice parameter of a cubic substance is directly proportional to the spacing 'd' of any particular set of lattice planes $a = d\sqrt{\left(h^2+k^2+l^2\right)}$ [24]. The Nelson–Riley method was used to minimize errors caused by aberration of 2θ variation and the lattice parameter 'a' of TiC was calculated for at least three peaks, using Eq. (1) [25].

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

The Williamson–Hall method was used to evaluate the grain size using Eq. (2) [26]. This method is based on broadening of the diffraction lines due to the internal strain and grain size.

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

Where 'θ' is the position of peak in the pattern (rad), 'd' is the grain size, 'ε' is the strain in the powder, 'λ' is the wavelength of the radiation used (nm) and 'b' is the full width at half maximum (FWHM) of the diffraction peak (rad). Silicon standard sample with large grains and free from defect broadening was used as a standard to increase the precision of the instrumental broadening. Then, the error of diffractometer was eliminated by Eq. (3) [27].

$$b = b_{size} + b_{strain} = \sqrt{b_o^2 - b_s^2} \quad (3)$$

where 'b_s' is the FWHM of the main peak of Si standard sample (2theta = 28.5°) used for calibration and 'b_o' is the FWHM of TiC's peaks. Both 'b_s' and 'b_o' were calculated by X-Pert High Score software.

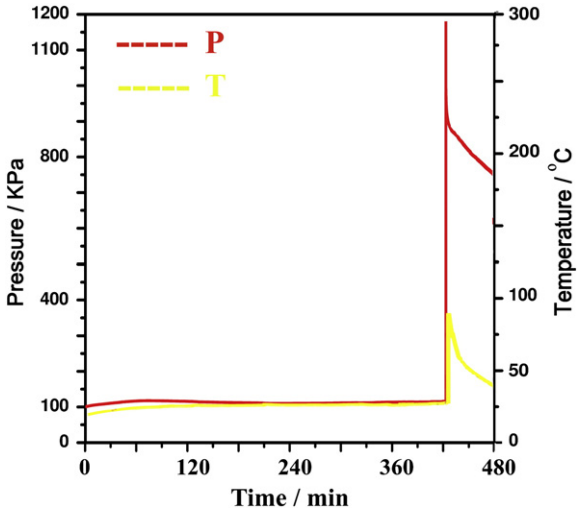

Fig. 2. Environmental changes of vial during milling of Ti and C powders (T: temperature and P: pressure).