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Ceramics International 39 (2013) 6703–6706

CERAMICS INTERNATIONAL

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Single step synthesis of tungsten carbide (WC) nanoparticles from scheelite ore

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Received 6 October 2012; received in revised form 26 January 2013; accepted 26 January 2013
Available online 5 February 2013

Abstract

To prepare tungsten carbide (WC) nanoparticles high purity precursors like W, WO_3, WCl_4, WCl_6 and $W(CO)_6$ are used. Moreover, these precursors are obtained after high temperature and multistage processing of the ore. In this article a single step synthesis method is reported to get tungsten carbide (WC) nanoparticles directly from scheelite ore. The mixture of scheelite, activated charcoal and magnesium was heated for 20 h at 800 °C in an autoclave which led to the direct conversion of scheelite to nanocrystalline WC. The undesired reaction products and impurities (CaO, MgO and SiO_2) were washed firstly with dilute HCl (1:1) and then with base (0.25 M NaOH). The obtained powders were characterized by high resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM) and X-ray diffraction.

Keywords: B. Electron microscopy; B. X-ray methods; Tungsten carbide

1. Introduction

Nano size WC has drawn considerable attention in scientific community because of their enhanced tribomechanical and chemical properties. Its suitability in fuel cell has opened new area of catalytic application for power generation [1,2]. Nano WC is found to possess bulk modulus comparable to that of diamond and is being used in high pressure experiments [3]. The major chunk of industrially produced WC goes into fabrication of cemented carbide for use in cutting tools, drilling and tunneling, dies, wear resistance parts etc. Worldwide annual production of tungsten for use in tungsten carbide is more than 70,000 t [4]. However, the synthesis routes followed for the preparation of nano WC are from pure precursors which makes the product costly and puts it on a scale of restricted application. Nanocrystalline WC has been synthesized from precursors like (i) WO_3 [5–9] (ii) elemental W [10] (iii) WCl_6 [11] (iv) WCl_4 [12] (v) $W(CO)_6$ [13]. These precursors are of high purity and obtained by processing of the ore at high temperature and moderate pressure where several intermediate steps are involved.

Although, more than 30 minerals of tungsten are known but only two of them—wolframite ($Fe,Mn(WO_4)$) and scheelite ($CaWO_4$) are important for extraction of tungsten [14]. World's largest deposits of tungsten are in China, followed by Canada, Russia, Australia, Korea, Turkey, Bolivia, Portugal and others, and 70% of reserves are in the form of scheelite mineral. Scheelite ($CaWO_4$) mineral is having tetragonal crystal structure. Its cell parameters are $a=5.24$ Å, $c=11.37$ Å with cell volume $=312.53$ Å^3. It occurs as contact metamorphic skarns, in high temperature hydrothermal veins and also as pegmatite.

Processing of the scheelite ore starts with its digestion in acid followed by base treatment to get Na_2WO_4 solution for purification [14–16]. The Na_2WO_4 solution is filtered and treated with $CaCl_2$ to form synthetic scheelite. The latter is then converted into tungstic acid by treating with HCl. Tungstic acid is further dissolved in ammonium hydroxide, and the solution after purification is crystallized to ammonium paratungstate (APT). WO_3 obtained after calcination of APT is further reduced to elemental W at high temperature (600–1100 °C) in H_2 atmosphere.

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http://dx.doi.org/10.1016/j.ceramint.2013.01.109

Elemental tungsten is the main source of other pure compounds like $W(CO)_6$, WCl_6 and WCl_4. This entire extraction process involving multiple treatments makes the final product (WC) costly.

Recently we have reported direct synthesis of WC nanoparticles by solid state reaction between scheelite and activated charcoal at 1025 °C in argon atmosphere [17]. In a quest to find out lower temperature method from an ore, a new route has been successfully attempted. The mixture of scheelite, activated charcoal and Mg in measured quantities was found to produce nanocrystalline WC at 800 °C in an autoclave. To the best of our knowledge, this is the first report on synthesis of single phase nanocrystalline tungsten carbide directly from the scheelite ore at 800 °C.

2. Experimental

The scheelite ($CaWO_4$) ore was procured from North American Tungsten Corporation, Canada. The major impurities in the ore were Fe (1.5–3.5%), SiO_2 (0.7–1.2%), Na (0.5%), S (0.2–1.0%), Al (0.1–0.2%), Bi (0.1–0.6), Mg (0.15–0.30%), Mn (0.15–0.30%), and rest impurities were at ppm level. The raw scheelite was milled for 50 h to reduce particle size. The charge to ball ratio was kept at 50:1. The activated charcoal (solid) and Mg (turnings) was used in as received condition. The experiment was performed using 1 g of milled scheelite, 2 g of activated charcoal and 1 g of Mg in a specially designed thick walled autoclave of SS 304 material. The sealed autoclave was kept in a furnace at 800 °C for 20 h. The furnace was heated at the rate of 5 °C/min. After the experiment, autoclave was allowed to cool in the furnace. The powders were taken out and washed with dilute HCl (1:1) to remove CaO, MgO and other impurities. The acid washed powders are designated as sample A in this paper. Finally the sample A was base treated (0.25 M NaOH) to remove traces of silica and designated as sample B.

The scheelite, sample A and B were characterized by X-ray diffraction (PANalytical) using Cu Kα (λ=1.54060 Å) radiation. The morphology of the powders were examined with field emission SEM (JSM 7600F). The high resolution transmission electron microscopy was done on JEOL-JM 2100F operated at 200 KV. For TEM study the powder was dispersed ultrasonically in ethanol. One drop of solution was taken on carbon coated copper grid and ethanol was allowed to evaporate.

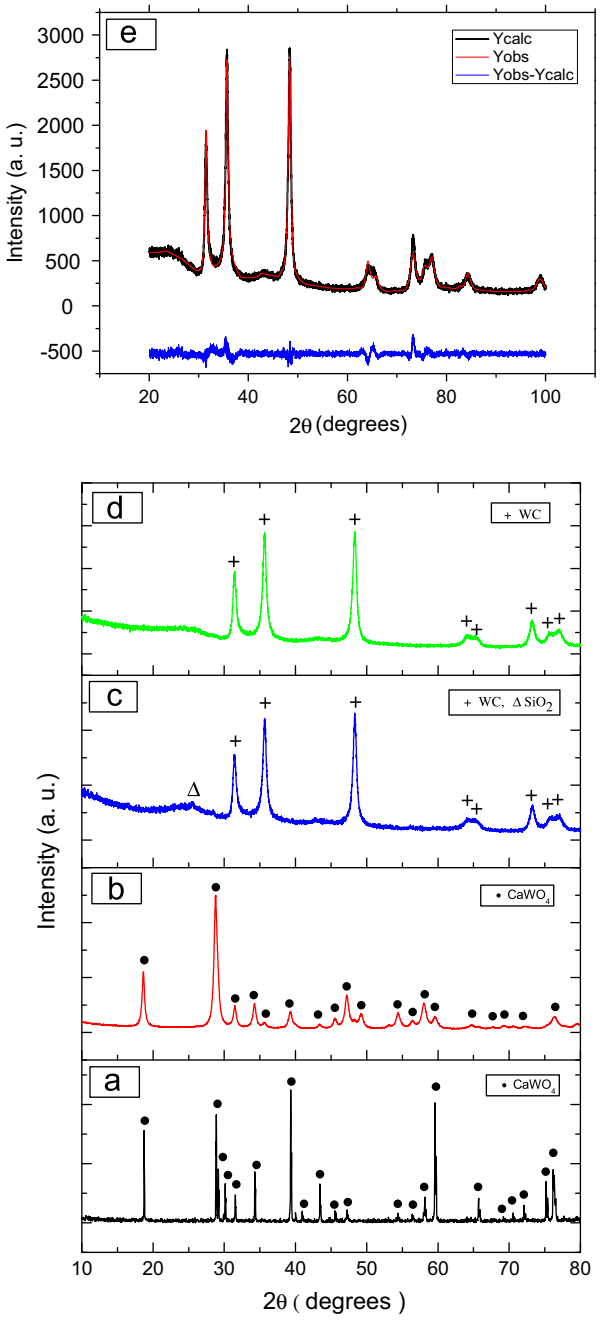

Fig. 1. X-ray diffraction pattern of (a) raw scheelite (b) scheelite milled for 50 h (c) sample A showing presence of WC and minor SiO_2 phase (d) sample B showing single phase nanocrystalline WC (e) Rietveld refinement plot of observed, calculated and difference profile of single phase nanocrystalline WC (sample B).

3. Results and discussion

Fig. 1(a) and (b) shows the X-ray diffraction pattern of raw scheelite and scheelite milled for 50 h. Fig. 1(c) shows the X-ray diffraction pattern of the sample A. The X-ray diffraction pattern matches well with WC (ICDD card no. 01-072-0097) and confirms the direct formation of nanocrystalline WC from scheelite. The crystallite size calculated from scherrer formula is 16 nm. The X-ray diffraction pattern of sample A also showed traces of SiO_2. This silica was removed by further washing with 0.25 M NaOH solution. The X-ray diffraction pattern was refined by Rietveld using Fullprof setup. The crystal structure showed $P\text{-}_6 m2$ symmetry with space group 187. The refined parameters are a=2.9032 Å and c=2.8400 Å with cell volume V=20.73 Å^3, the parameters shows good fit with Chi Square (χ^2)=2.01 as shown in Fig. 1(e).

Fig. 2(a) and (b) shows HRSEM of sample B. The two different types of structural features are visible in the micrographs. The dark color particles having flake type

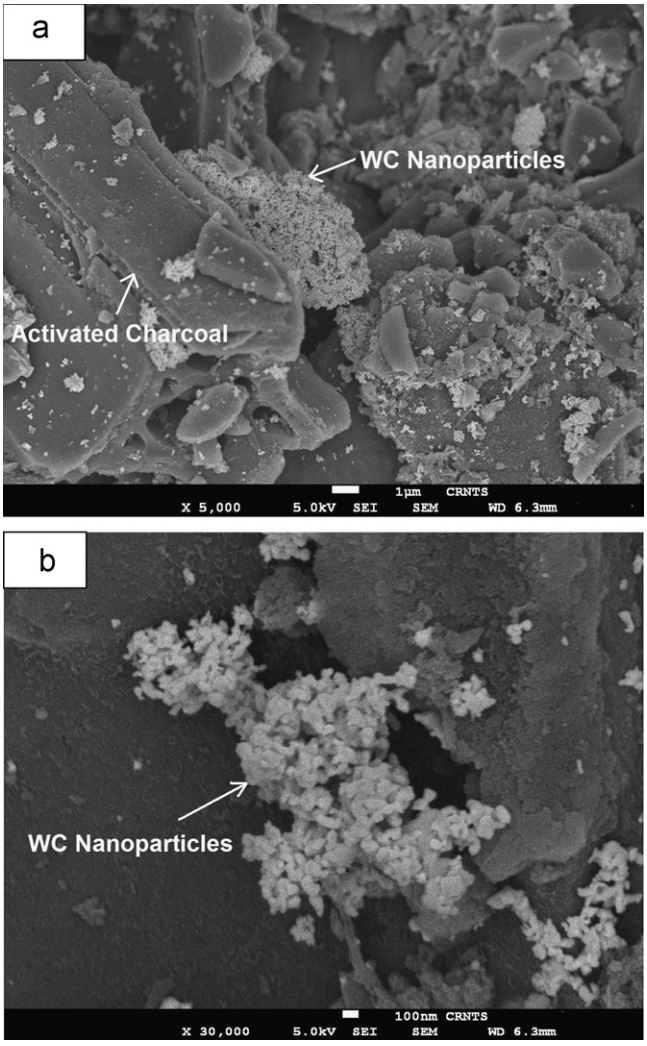

Fig. 2. (a) and (b). HRSEM of sample B showing WC nanoparticles and activated charcoal.

features is charcoal. The white colored nanoparticles are of tungsten carbide. The solid gas phase reaction taking place in the autoclave has led to formation of nanocrystalline WC. The possible reaction mechanism is given below:

$$CaWO_4 + Mg \rightarrow W + MgO + CaO \quad (1)$$

$$2C + O_2 \rightarrow 2CO \quad (2)$$

$$2W + 2CO \rightarrow 2WC + O_2 \quad (3)$$

the magnesium is reducing the $CaWO_4$ to W at 800 °C. As there is excess carbon in the autoclave so activated charcoal forms CO gas. This CO reacts with elemental tungsten to produce WC. The oxygen evolved further reacts with C to form CO and this cycle goes on till the entire W is carburized. The impurities present in the ore provide the site for breakage of scheelite at high temperature and pressure. The high pressure developed in the autoclave facilitated diffusion of carbon to get WC nanoparticles [18–21].

Fig. 3(a) shows the HRTEM of sample B. The tungsten carbide crystals are in agglomerated form due to high surface area. Fig. 3(b) shows the lattice fringes of nanocrystalline WC particles. The d-spacing is found to be 0.26 nm and 0.18 nm which is for (100) and (101) plane of WC (ICDD card no. 01-072-0097) respectively.

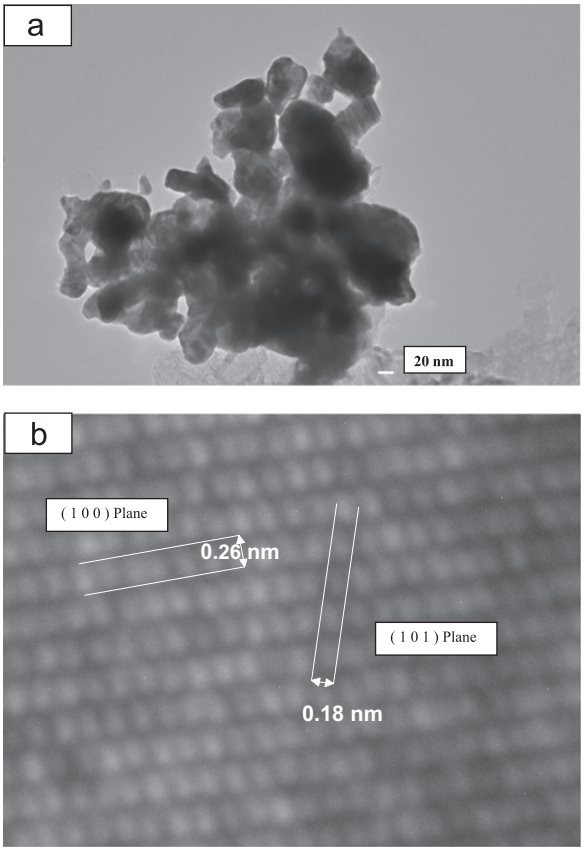

Fig. 3. HRTEM of (a) sample B (b) lattice fringes of WC nanoparticle.

For the extraction of W and synthesis of other tungsten precursors multi step and high temperature treatments are followed in the industries which make the entire process costly. Here, in our present study, we have exploited acid resistant property of WC for this non conventional method of synthesis. Since WC is resistant to HCl attack, the major impurities can be leached out from the mixture of nanocrystalline WC and ore impurities. Furthermore, these impurities act as stress centers which facilitate the cracking of scheelite ore. Later on these impurities along with other reaction products like CaO and MgO are washed out by dilute acid and base. Here in this process, consumption of chemicals as compared to the industrial process is very less, since only impurities and compounds CaO and MgO are to be washed and not the whole of the ore is to be digested [16]. Furthermore it is generating lesser effluent. This is an economical and eco-friendly method best suited for industrial bulk production of WC nanoparticles.

4. Conclusions

For the first time single phase nano crystalline WC has been successfully synthesized directly from scheelite, an ore of tungsten (W) at 800 °C. The impurities present in the

ore may help in retaining nano size which are leached out after synthesis. This route is environment friendly, generating lesser quantity of effluent than conventional process. This study may open up more research routes to synthesize nanocrystalline carbides and other advanced materials from ores or impure compounds.

Acknowledgment

The authors are grateful to Dr. A.R. Kulkarni, IITB and Mr. Rajan, IITB for help in HRSEM analysis. Harjinder Singh thanks to Dr B. N. Chudasama and Ms Samita for help in Rietveld analysis. The financial assistance provided by Department of Science and Technology, New Delhi, India vide letter no. SR/S3/ME/0037/2009-SERC dated 15/07/2010 is highly acknowledged.

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