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Synthesis of nanostructured tungsten carbide via metal-organic chemical vapor deposition and carburization process

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ABSTRACT

Nanostructured tungsten carbide particles were successfully synthesized by metal-organic chemical vapor deposition in a spouted bed followed by carburization in CH_4/H_2 atmosphere in the temperature range 700–900 °C. The carburization process was a little bit complex, which involved the coating of carbon on the outer surface of the decomposed $W(CO)_6$ precursor particles and then followed by carbon diffusion into the particles, leading to the formation of nanostructured WC via an intermediate metastable phase W_2C. The carbon deficient phase W_2C was formed initially at lower carburization temperature and then transformed to stable WC phase by increasing the temperature and holding time.

Introduction

Tungsten carbide (WC) is considered to be an excellent ceramic material because of its unique combination of properties viz. high young's modulus (550 GPa), high melting point (2870 °C), extremely high density (15.63 g/cm^3), and excellent abrasive and corrosion resistance [1–4]. Nanostructured WC has taken more attention since a few decades due its application for cutting tools and wear-resistant components [5,6]. It also exhibits high fracture toughness, which is helpful for the mechanical and tribological applications [7,8].

There are several reports available regarding the synthesis of nanocrystalline WC. Room temperature synthesis of nanocrystalline WC from a blend of tungsten and carbon powder by high energy ball milling has been reported in [9]. Such low temperature phase formation has been attributed to enhanced diffusivity in nanocrystalline structure [10]. Some other methods such as thermal plasma processing of WCl_6 under hydrogen atmosphere [11], pulsed discharge of bulk W and graphite rods immersed in pure ethanol [12] as well as co-reduction of WCl_6 and sodium carbonate with metallic magnesium at 873 K in autoclave [13] have been developed for the synthesis of nanostructured WC powder.

All the methods reported above are associated with single step process. However, there also exists two-step process, where tungsten oxide is first reduced to tungsten in hydrogen atmosphere, and subsequently blended with carbon and carburized at 1673–1873 K [14]. Recently, Kumar et al. [15] have shown that the reduction and carburization of WO_3 to WC are possible at around 873 K by thermochemical reaction in an autoclave in the presence of Mg, ethanol and acetone. The carburization of tungsten oxide is a complex process considering the fact that the final product could be WC_{1-x}, W_2C or WC depending on the processing parameters. Koc and Kodambaka [16] have reported tungsten carbide formation from a precursor comprising of WO_3 coated with excess of carbon derived from pyrolytic cracking of propylene (C_3H_6). The formation of W_2C followed by WC was observed under argon atmosphere while only WC evolved when the heat treatment was performed under H_2. Although lot of research work has been carried out on synthesis of nanostructured WC, the precursor carburization of amorphous WO_3 nanopower in order to get nanostructured WC is still under study.

In the present work, nanocrystalline WC powders have been synthesized by metal-organic chemical vapor deposition (MOCVD) method in a spouted bed followed by carburization in CH_4/H_2 atmosphere. Initially, the pyrolysis of tungsten hexacarbonyl $W(CO)_6$ precursor produces amorphous nano-powder of WO_3. In the later stage, it transforms into nanocrystalline stable WC via an intermediate phase W_2C upon carburization. The microstructure and phase transformation mechanism of WC have been investigated in detail.

Experimental details

Pyrolysis of $W(CO)_6$ precursor

Tungsten hexacarbonyl ($W(CO)_6$, 99%, Acros Organics Co., USA) was taken as the precursor of WO_3 in the MOCVD process. This experiment

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was performed in a glass tube passing through a heated furnace. The carrier gas of high-purity helium (99%) was fed through a heated bubbling unit containing the metal organic precursor at the vaporization temperature of 90 °C and flow rate of 10 ml/min in the spouted bed reactor. The precursor was decomposed in the spouted bed at 300 °C with the deposition time of 1 h. The detail about the apparatus has been described in our previous work [17].

Carburization treatment

The decomposed precursors obtained from pyrolysis at 300 °C were annealed in a reaction furnace under constant gas flow (CH_4:H_2 = 1:9) at various temperatures in the range 700 to 900 °C. The flow rate of Ar gas was 50 ml/min and the carrier gas maintained the methane and hydrogen flow uniformly in the furnace. All of the samples were carburized by varying the dwell time (0 to 5 h) followed by furnace cooling to the room temperature.

Characterization techniques

After carburization treatment, the specimens were characterized by the X-ray diffraction (Rigaku D/max-II B, Japan) with Cu Kα radiation (λ = 1.5405 Å) at room temperature. XPS measurements were performed with a VG Scientific model 210 spectrometer equipped using Al Kα monochromatic X ray source (1486.7 eV) with 25 W X-ray power. Transmission electron microscopy (JOEL 2010-A, Japan) measurements were performed on carburized samples along with EDS and selected area diffraction pattern (SADP) to identify different phases of tungsten carbide.

Results and discussion

Characterization of decomposed precursors

In order to confirm the nature and to calculate the particle size of the decomposed precursors, TEM measurement has been carried out on the decomposed powder as given in Fig. 1a. The diffraction pattern shown as inset clearly confirms that the powder is amorphous and the particle size is found to be less than 50 nm. The XPS results shown in Fig. 1b indicate the binding energy difference about 2.15 eV between the W-4$f_{5/2}$ and W-4$f_{7/2}$ states, which corresponds to WO_3 [18]. From EDS analysis on a selected grain in the TEM image, the composition of the amorphous nanopowder is found to be a mixture of carbon and WO_3. The pyrolysis of the $W(CO)_6$ precursor can be described by the following equation:

$$W(CO)_6 \rightarrow W + 6CO. \quad (1)$$

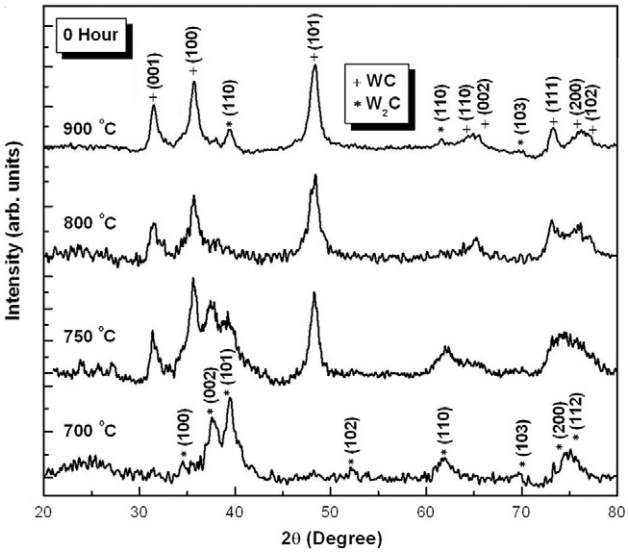

Fig. 2. XRD patterns showing carburization of as-deposited precursor $W(CO)_6$ powder at different temperatures in the range 700 to 900 °C without isothermal holding.

Kriss and Meda [19] have indicated that when the $W(CO)_6$ decomposes at a temperature lower than 300 °C, the crystal structure shows amorphous behavior. Then the W metal gets oxidized with the partial pressure of oxygen at lower vacuum [20].

Carburization of decomposed $W(CO)_6$ powder

Fig. 2 shows the XRD patterns of decomposed precursor $W(CO)_6$ powder at different carburization temperatures (700 to 900 °C) without any holding time (0 h). It is observed that the two phases of tungsten carbide i.e. W_2C and WC evolved with reference to different annealing conditions. At lower carburization temperature (700 °C), only W_2C phase is found to be present, whereas WC phase starts to appear at 750 °C along with W_2C. Further increase in temperature to 800 and 900 °C, leads to the appearance of mostly WC phase, because WC exists as the stable form in the temperature range of 800 °C to 1850 °C [21] and below 1250 °C [22]. Additionally, free energy of WC has a more negative value that W_2C below 1100 °C, implying WC to be more stable phase compared to W_2C [23]. However, a small amount of W_2C still exists at 900 °C. The formation of little WC phase below 800 °C and W_2C phase above 800 °C may be due to the intermixing W_2C and WC at this temperature. From the above results, it is concluded that with the

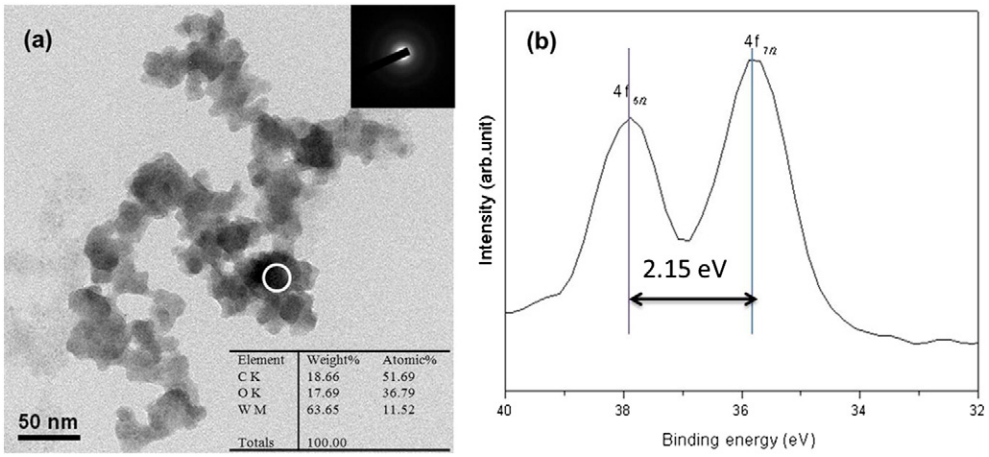

Fig. 1. TEM micrograph (a) and XPS spectrum (b) of decomposed $W(CO)_6$ precursor powder.