New processing method for tungsten carbide nano-crystalline particles and nano structural carbon via polyacrylonitrile gasification

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A simple processing route has been developed for a nano-sized crystalline tungsten mono-carbide (WC) and a novel nano-structural carbon materials. Starting materials for WC synthesis were selected tungstic acid (H_2WO_4) and polyacrylonitrile (PAN) powders. The starting powders were heat-treated at 1200°C for 30 min with a nitrogen gas flow in an alumina tube. The acquired WC powder had a nano-sized crystalline and high-specific surface area ($26.0 \text{ m}^2 \text{ g}^{-1}$). Crystallite diameter size was estimated to less than 20 nm. Compared with theoretical value, approximately 2.0 mass % of free carbon was measured in the prepared WC. It was observed that layered graphitic carbon was formed around the WC particles. If the graphitic carbon is separated from the WC particles by appropriate techniques or processing conditions, these techniques using PAN as a carbon source may have possibility for processing not only WC but also nano-structural carbon materials such as graphene.

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1. Introduction

Tungsten carbide (WC) finds potential applications owing to its unusual properties, such as high melting point, superior hardness, low friction coefficient, high oxidation resistance, and superior electrical conductivity.¹⁾ There are several routes to prepare tungsten carbide materials, including the direct carburization of tungsten metallic powder, solid-state metathesis, reduction carburization, mechanical milling, and polymeric precursor routes using metal alkoxides.^{2,3)} Generally, Tungsten carbide production proceeds as a two-step process. First, the tungsten oxide is reduced to high-purity tungsten in a hydrogen atmosphere. The tungsten metal is then mixed with the required amount of carbon and reacts at a temperature of 1400–1600°C to produce tungsten carbide in a hydrogen atmosphere.^{4,5)} The most important tungsten carbides are WC and W_2C . W_2C is thermodynamically unstable at low temperatures, while WC is stable, as confirmed by its electrochemical stability in acidic solutions.⁶⁾

WC was shown to have platinum (Pt)-like behavior for the chemisorptions of hydrogen and oxygen, and its applicability as an alternative electro-catalyst of Pt was demonstrated.⁷⁾ The early studies showed that this combination of an early transition metal with carbon yielded materials with attractive catalytic activity, stability, selectivity, and resistance to poisoning.⁸⁾ Recently, WC has been considerably studied in hydrogenation, dehydrogenation, isomerization and fuel cells because of its Pt-like catalytic

activities, excellent stability and CO poisoning tolerance.^{7–11)} The catalytic activity and stability of pure WC can be further improved by formation of WC-containing composites, such as WC-silica,¹²⁾ and WC-carbon.¹³⁾

Graphitic carbon (GC), for example, carbon nano-tubes, nano-capsules and nano-sheets, have found wide application in synthesis of nano-composites due to their superior physical and chemical properties.^{14,15)} Several researchers have demonstrated that the combination of WC with GC could improve catalytic capability.¹⁶⁾ Nevertheless, these methods are restricted to the use of pre-synthesized GC that need to be purified, functionalized and impregnated with tungsten precursor, followed by heating treatment at different atmosphere.^{17–19)} Furthermore, they often suffer from the aggregation of WC particles, leading to the loss of activity and stability. Therefore, it is fairly attractive to develop a simple and general approach for the synthesis of a WC/GC composite with highly active, stable and well-dispersed WC.

Recently, several methods have been reported to obtain transition metal carbide nano-particles.²⁰⁾ However, the route to tungsten carbide nano-particles through organic compounds and tungsten oxides has been rarely investigated. We design a highly efficient and facile reaction route assisted by carbothermal reduction to prepare tungsten carbide nano-particles. It is well known that polyacrylonitrile (PAN) is one of precursor materials for pyrolytic carbon, glassy-like carbon and carbon fiber. Especially, well graphitized carbon fiber was extremely attracted materials by reason of their high strength and flexibility.²¹⁾ Therefore, PAN was expected for appropriate carbon source to synthesize WC or WC/GC composite materials.²²⁾

In this study, it is explained that a novel processing method for WC particles with nano-sized crystallite and residual carbon with nano-architecture derived from PAN.

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2. Experimental procedure

Starting materials for WC synthesis were composed of tungstic acid powder (H_2WO_4) as a tungsten precursor and polyacrylonitrile powder [PAN: $(\text{CH}_2\text{CHCN})_n$] as a carbon precursor. Weight ratio of PAN/ H_2WO_4 was changed in the range of 1.0 and 4.0. Each of the starting powder was separately set on carbon boats. These powders set on a carbon boat were heat-treated with a nitrogen gas flow (50 mL min^{-1}) in an alumina tube. The 1000 mm long alumina tube was placed in an electrical resistance furnace and thermally treated at 1200°C with a heating rate of 10°C/min for 30 min. After a given reaction time, the furnace was cooled naturally to room temperature. Then product samples were obtained.

The phase compositions were identified by X-ray diffraction Patterns (XRD: Miniflex2, Rigaku, Japan) at 30 kV and 15 mA of Cu K α radiation. Specific surface areas of the products were measured using the BET method (Bellsorp mini, Japan). In order to characterize the products surfaces, the morphologies of the obtained materials were observed by using an scanning electron microscopy (SEM: 30 kV, S-4800 Hitachi, Japan), transmission electron microscopy (TEM: 200 kV, JEM-2000FX JEOL, Japan) and high resolution transmission electron microscopy (HRTEM: 200 kV, JEM-2100F JEOL, Japan). The microprobe instrument used for the FT Raman spectroscopy consisted of a spectrometer (JOBIN YVON-HORIBA SPEX) fitted with an optical microscope. The 632.8 nm line of a He-Ne laser was used as excitation, focused in a spot of approximately $10 \mu\text{m}$ diameter, with an incident power of 2 mW.

3. Results and discussion

XRD patterns of the obtained powders in PAN/ H_2WO_4 weight ratio of 3.0 were shown in Fig. 1. The distinct diffraction peaks at $2\theta = 31.5$, 35.7 and 48.4 degrees are indexed as the (001), (100) and (101) planes of hexagonal WC phase, respectively. The results show that WC has been successfully synthesized in more than 3.0 of PAN/ H_2WO_4 weight ratios. However, no significant diffraction peak at $2\theta = 26.2$ degrees was characteristic of the graphite. From the BET test results, calculated specific surface area was approximately $25.0 \text{ m}^2 \text{ g}^{-1}$ in this fully synthesized WC particle (PAN/ $\text{H}_2\text{WO}_4 = 3.0$). According to this specific surface area, the estimated average particle size was approximately 15.4 nm. The crystallite diameter was estimated to approximately 13.3

Fig. 1. X-ray diffraction patterns of obtained products (PAN/ H_2WO_4 weight ratios: 3.0).

nm from the XRD pattern, as shown in Fig. 1, by Scherrer's equation written in follows:

$$D = K\lambda(\beta \cos \theta)^{-1} \quad (1)$$

where crystallite diameter: D , $K = 0.94$, $\lambda = 0.154178 \text{ nm}$ (Cu K α) and β = (Full Width Half Maximum).

SEM micrographs of the synthesized WC material (PAN/ $\text{H}_2\text{WO}_4 = 3.0$) were shown in Fig. 2. It was revealed that the observed WC particle had a nano-sized crystalline and plate or needle like structure, as shown in Figs. 2(a) and 2(b). The observed particle size was estimated about 300 nm length and 30 nm width. It was observed that the nano-sized crystalline WC

(a)

(b)

(c)

Fig. 2. (a) SEM micrographs of synthesized WC using PAN (BET area = $25.0 \text{ m}^2 \text{ g}^{-1}$). (b) SEM micrographs of synthesized WC using PAN (BET area = $25.0 \text{ m}^2 \text{ g}^{-1}$). (c) SEM micrograph of employed H_2WO_4 powder (BET area = $20.7 \text{ m}^2 \text{ g}^{-1}$).

Fig. 3. TEM image of the obtained WC particles.

was aggregated, as shown in Fig. 2(a). This aggregation may be derived from excessive carbon in the products.¹⁶⁾ Surface morphology of the using H_2WO_4 powder was shown in Fig. 2(c). The H_2WO_4 starting powder had a nano-sized crystalline and plate or needle like structure. It was supposed that the obtained WC had similar surface morphology of the H_2WO_4 starting powder. Therefore, in order to give more fine architecture to WC, particle size controlling of H_2WO_4 could be important. Graphitic carbon nitride can further release some chemically reactive hydrogen-, carbon- and nitrogen-containing atomic species over 600°C from the PAN. These highly active carbon nitride or atomic nitrogen species may play triple roles as the reduction, nitridation and carburization reagent. Firstly, these chemically active species will reduce the tungsten oxides into the corresponding active tungsten atoms. Secondly, these active metal atoms will further react with carbon nitride species to form tungsten nitrides. Finally, with increasing temperature, the subsequent carburization processes between the tungsten nitrides and carbon nitride species will occur and lead to the corresponding carbides. The overall reaction processes can be speculated above described. Consequently, the final products were processed as WC.

It was revealed that crystallite diameter of the obtained WC materials was under 20 nm and the WC particles were aggregated or partially sintered through TEM observations, as shown in Fig. 3. No residual free carbon was clearly observed in the TEM image. However, it was observed that residual free carbon surrounded the WC nano crystalline particles within a HRTEM image, as shown in Fig. 4. Moreover, that the carbon surrounded the WC particles was graphitized because the carbon had layered construction which distance between the each layer was 0.34 nm. This value is same of graphite materials. There was no significant peak of crystalline carbon in the XRD pattern at $2\theta = 26.2$ degrees, as shown in Fig. 1. However, it was detected that clear peaks derived from crystalline carbon at 1360 and 1580 cm^{-1} in Raman spectra, as shown in Fig. 5. It was supposed that the two significant peaks in the Raman spectra were derived from crystalline carbon surrounding the WC nano-particles. It was well known that nano-structural carbon materials like as carbon nanotube (CNT) was made by using transition metal catalyst,²¹⁾ and that WC was shown to have platinum (Pt)-like behavior for the chemisorptions of hydrogen and oxygen, and its applicability as an alternative electro-catalyst of Pt was demonstrated.⁷⁾ Consequently, it was guessed that the obtained WC particles might play a role of catalyst for the observed nano-structure as shown in Fig. 4.

Fig. 4. HRTEM image of the obtained WC particles.

Fig. 5. Raman spectra of obtained product surface (PAN/ H_2WO_4 weight ratios: 3.0).

Weight of the products was approximately 2 mass % greater than that of theoretical calculation, which product was only WC. It was presumed that the excessive weight was free carbon. If the free carbon adsorbed on the WC particles surface has well oriented architecture or is fully graphitized, it is expected that specific surface area is made more increasing and favorable for high catalytic activity and stability.¹⁶⁾ Further development is needed for synthesizing a WC/GC composite material (higher temperature treatment, under vacuum environment etc.). Resultant WC materials had a nano-sized crystalline phase and high surface areas. Hydrogen treatment should be conducted as needed for removing free carbon from the synthesized products.²³⁾ Nevertheless, above shown nano-sized crystalline and specific surface area indicates possibility for enhancing catalytic properties and developing cutting machine tools. The easy one-step method using PAN gasification gas as a carbon source can be candidate of a new processing route for a nano-sized tungsten mono-carbide material. Meanwhile, it is known that transition metal carbide like as WC materials can be dissolved in hydrogen peroxide (H_2O_2) solution.²⁴⁾ If the observed graphitic carbon is separated from the WC particles by appropriate techniques or processing conditions, the employed techniques using PAN may have possibility for processing not only WC but also nano-structural carbon materials such as graphene materials.

4. Conclusions

Single phased and nano-crystalline WC has been successfully synthesized in PAN/H₂WO₄ weight ratios of more than 3.0. The acquired WC powder had a nano-sized crystalline and high-specific surface area. Crystallite size was easily estimated to less than 20 nm. Compared with theoretical value, a few mass % of free carbon was measured in the prepared WC. Surface of the WC particles was wrapped by carbon. It was observed that layered structure like as graphite was formed around the WC particles. It is needed that the free carbon is removed from the WC particles by appropriate processing conditions. The employed techniques using PAN as a carbon source may have possibility for processing not only WC but also graphene materials.

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