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Original Research Paper

Synthesis of metastable cubic tungsten carbides by electrical explosion of tungsten wire in liquid paraffin

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ABSTRACT

This paper describes experiments addressing the synthesis of WC_{1-x} (metastable cubic tungsten carbide). The experiments involved exploding tungsten wires of different diameters by passing high-current electric pulses through them. This was done while the wire was immersed in a liquid-paraffin media. The explosion was studied using a high-speed video camera and by analysis of the voltage and current signals. The different stages of the wire explosion were explained based on an analysis of the recorded signals and simple thermodynamic considerations. In most of the experiments, the wire was sublimated, and the formation of carbide particles occurred due to a chemical reaction between the explosion products and the paraffin, as well as the rapid condensation of the vapors. The synthesized powders were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron probe microanalysis (EPMA). It was found that, regardless of the experimental conditions, the WC_{1-x} phase contained approximately 42.5 at.% carbon. If the energy injected into the wire was not sufficient to completely evaporate the tungsten, large particles consisting of WC, W_2C, and W phases were formed via the liquid-state diffusion mechanism.

1. Introduction

According to the tungsten-carbon phase diagram, three types of tungsten carbide may exist in a system: WC, W_2C, and WC_{1-x} [1]. Among these, only the WC compound with a hexagonal unit cell is stable at low temperatures. This compound is also the most widely used in industry and particularly in powder metallurgy. Possessing an extraordinarily high level of hardness, it is used as the main component of WC-Co cemented carbides [2]. The other two compounds, hexagonal W_2C and cubic WC_{1-x}, have attracted less attention for mechanical engineering applications due to their high brittleness. However, WC_{1-x} has been found to possess some interesting physical and chemical properties which make it attractive for applications in other fields of industry. For instance, according to a thermodynamic analysis undertaken by Suetin et al. [3] the density of the states near the Fermi levels of WC_{1-x} is almost double that of W_2C and six times higher than that of WC. Based on this concept, Kim et al. synthesized a WC_{1-x}/Pt/carbon nanotube catalyst which exhibited catalytic properties that were superior to those of a Pt/carbon nanotube catalyst [4]. That study, as well as the promising results related to photo- and electro-catalytic activity obtained by Hara et al and Zheng et al. [5,6], have led to the chemical properties of WC_{1-x} currently being of great interest to researchers. Pawlak et al. showed that WC_{1-x} coatings significantly improved the wear-resistance properties of Ti substrates [7]. In a brief review of a W–C system, Kurlov and Gusev noticed that the WC_{1-x} phase has the highest superconducting transition temperature out of three known types of tungsten carbide [8]. An analysis of the W–C phase diagram reveals that the WC_{1-x} phase is stable only over a temperature range of 2530–2747 °C. Thus, being metastable at room temperature, this compound does not typically appear as a result of convenient chemical processes like the carburizing of elemental tungsten or tungsten oxide. However, it can be obtained at room temperature by the rapid solidification of the melt if the cooling rate is sufficiently high. For instance, Demetriou et al. and Zhang et al. found that this compound could be obtained by the rapid solidification of the melt at a cooling rate of 10^8–10^{11} K/s [9,10]. Such high cooling rates are typically achieved when a very thin layer containing the WC phase is remelted and crystalizes

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on the substrate [10,11]. Another approach, which may be used to obtain metastable powders, is the wire explosion process (WEP), which is also known as a pulsed wire discharge (PWD) or electric explosion of wires (EEW) process. WEP, EEW, and PWD are single-step cost-effective techniques for synthesizing nanoparticles [12]. By appropriate selection of the explosion environment, it is possible to initiate a chemical reaction between the explosion products and the surrounding atmosphere. Thus, various chemical compounds can be synthesized using these techniques. Research on the synthesis of powders by wire explosion has been actively pursued over the past decade. Murai et al. produced organic-matter-coated copper nanoparticles that showed excellent oxidation resistance by the explosion of copper wires in an organic gas atmosphere [13]. Kurlyandskaya et al. produced a composite material composed of Ni nanoparticles and an acrylic copolymer possessing excellent microwave absorption properties [14]. Vykhodets et al. produced alumina nanopowders with extreme deviations from stoichiometry using laser vaporization of ceramic targets [15]. Kinemuchi et. al showed that aluminum nitride nanoparticles can be produced by the explosion of Al wires in nitrogen gas [16]. Similarly, tungsten carbide nanoparticles were obtained by using W wires in CH_4 gas [17]; zinc oxides particles by using Zn in oxygen gas [18]; and Cu-Ni-P alloy nanoparticles by using Cu, Ni and P wires in nitrogen gas [19]. Various liquid media can also be used to produce nanoparticles based on pure metals [20,21], nitrides [22], and carbides [23,24].

In the present study, the electrical explosion of elemental tungsten wires in liquid paraffin was analyzed. Different diameters of tungsten wires were used to find the optimal energy conditions for the explosion leading to the highest volume fraction of WC_{1-x}. The explosion process was visualized using a high-speed video camera while the current and voltage histories were recorded. The structures of the fabricated powders were characterized.

2. Experimental

The wire explosion experiments were performed in a stainless-steel container, shown schematically in Fig. 1. The tungsten wires (99.5 mass% tungsten) used in the experiments were provided by Niraco Co., Ltd. The container was filled with liquid paraffin provided by Nakarai Tesque Co., Ltd. (density = 0.86–0.88 g/ml), which provided the source of carbon. A high-voltage oil capacitor bank capable of storing up to 10 kJ of energy (capacitance = 12.5 μF, maximum charging voltage = 40 kV) produced by Nichicon Corporation was used to generate the high-current electric pulse. The changes in the current and voltage with time were measured using a Rogowski coil (current-monitoring Model 101 produced by Pearson Electronics, Inc.) and a high-voltage probe (EP-50K produced by Nissin Pulse Electronics Co., Ltd.,) attached to the cable. The signals from the high-voltage probe and Rogowski coil were recorded using a high-frequency digital oscilloscope (Tektronix, Inc., DPO7254C). The experimental parameters are summarized in Table 1. In the present study, the variable parameter was the wire diameter. By changing this parameter, it was possible to control the voltage across the wire, the current passing through it and thus the amount of electrical energy dissipated in the wire as a result of the explosion.

To observe the explosion in the liquid paraffin, a special container was prepared using transparent material (PMMA), and the process was observed using a high-speed video camera (Shimazu Co., Ltd., HPV-1). The frame rate was 1 million fps. The output voltage from the high-voltage probe was used to trigger the high-speed video camera.

To separate the synthesized powder, the liquid paraffin containing the explosion products was mixed with kerosene. The explosion products were then carefully filtered using a fine filter paper (GE Healthcare Ltd., Whatman Grade No. 5 Filter Paper). The fabricated powders were analyzed by X-ray diffraction (XRD) analysis using Cu-Kα_1 radiation with a Bragg-Brentano diffractometer (Rigaku Co., Ltd., Ultima IV), scanning electron microscopy (SEM; JEOL Ltd., JSM-6390LV), transmission electron microscopy (TEM; Philips TECNAI F20) and electron-probe microanalysis (EPMA; Shimazu Co., Ltd., EPMA-1720H) measurements. The elemental composition measurements and elemental mapping were performed using electron probe micro-analyzer.

Table 1
Experimental parameters.

Experiment #	Voltage (kV)	Wire length (mm)	Wire diameter (mm)
1	40	200	0.30
2			0.32[a]
3			0.50
4			1.00

[a] In this experiment, 10 wires each with a diameter of 0.1 mm were joined parallel to each other giving the same cross-sectional area as 1 wire with a diameter of 0.32 mm.

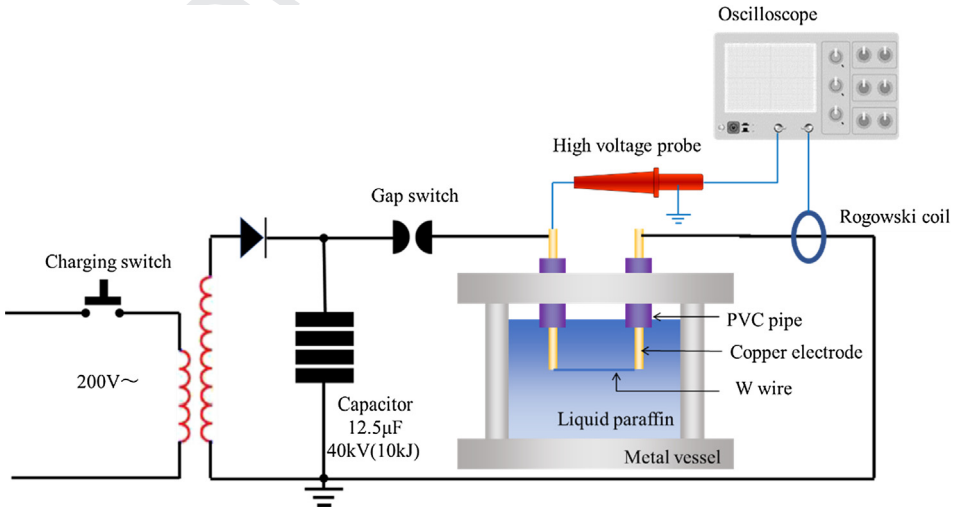

Fig. 1. Schematic illustration of experimental setup used to electrically explode wire.

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