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Original Research Paper

Effect mechanism of arsenic on the growth of ultrafine tungsten carbide powder

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ABSTRACT

Arsenic element refines W powders significantly during the hydrogen reduction process of tungsten oxide in our previous studies. In this paper, the nanocrystalline WC-As composite powders were prepared by carbonization of nano W-As composite powders and the effects of arsenic on the growth of WC powder were discussed in detail. The prepared samples were characterized by X-ray diffraction, differential scanning calorimetric analysis, scanning electron microscope, transmission electron microscope, X-ray photoelectron spectroscopy and Inductively Coupled Plasma. The results showed that arsenic appropriately raised the initial temperature of carbonization, significantly accelerated carbonization reaction process and shorten the reaction time. Moreover, WC-As composite powders merged and grew up directly without particle expansion and cracking. And the nano WAs_2 particles attached to WC grain boundaries and hindered the growth of WC grain through grain boundary migration. The above two effects resulted in the WC-As composite powders prepared at 1300 °C for 2 h with the average size of about 121 nm in diameter.

1. Introduction

Due to the unique properties such as high hardness, good corrosion resistance, high thermal and electrical conductivity, cemented carbide is commonly used in many important areas, such as machining, cutting, mining and drilling tools [1,2]. nano tungsten carbide (WC) powder is an important raw material for the preparation of ultrafine cemented carbide, which can produce hard alloy material with high hardness, high wear resistance and high toughness [3,4]. Arsenic is the primary impurity element and its content reached 0.3 wt% in wolframite or scheelite ores in the form of arsenate. Magnesium salt purification method is often used to remove arsenic during the preparation process of ammonium paratungstate (APT), and this process is very complicated [5,6]. However, we found that arsenic could be used as a beneficial element to prepared uniform nanocrystalline WC powder.

There are a number of processes for the synthesis of WC powders including direct carbonization of tungsten oxide [7], solid state metathesis [8–10], mechanical milling [11–13], plasma methods [14,15] and polymeric precursor routes using metal alkoxides [16]. However, these novel methods suffer from various disadvantages, including expensive equipment and the difficulty of controlling carbon content. Presently, WC powders are produced by direct carburization of tungsten powder. The W powder is mixed with 6.13 wt% carbon black and carbonized at above 1250 °C to prepare WC powder [17,18].

In this paper, the nanocrystalline WC-As composite powders with uniform distribution were prepared by traditional W powders carbonization method. A systematic study has been carried out to study the effects of arsenic on the formation and growth of WC at different carbonization temperature. Our research provides a new idea to utilize the impurity of As in the scheelite ores to produce uniform tungsten carbide powder by the traditional method of reduction-carbonization.

2. Experimental procedure

Nano W-As composite powder (particle size 80 nm) or pure W powder (particle size 1.321 μm) and carbon black were used as the raw materials of tungsten carbide powder. Firstly, W-As composite powder was mixed with carbon black by planetary ball mill

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at a speed of 100 r/min for 1 h. Both the jar and the milling balls are made of the agate. Then the W-As/C mixture powders were filled in a graphite boat and then pushed into the tube furnace for carbonization at 1300 °C, 1400 °C, 1500 °C and 1600 °C under hydrogen gas flow, respectively. The heating rate was controlled at 5 °C/min. Besides, glucose was also used as carbon source to analyze the thermal analysis process.

The phase composition of the powders was examined by X-ray diffraction (XRD, D8-Focus Bruker-AXS) using Cu-Kα radiation. The grain size of particles was calculated by the XRD data according to the Scherrer Formula. Differential scanning calorimetric analysis (DSC) was conducted on a STA–409PC/4/H Luxx simultaneous TG-DTA/DSC apparatus (Netzsch, Selb) with a heating rate of 10 °C/min under Ar atmosphere using Al_2O_3 as the reference. The morphology and microstructure of synthesized powders were characterized with a field-emission scanning electron microscopy (SEM, Nova Nano SEM 450 FEI) with energy dispersed spectroscopy (EDS, INCA Energy 250 X-max 50 Oxford Instruments) and a high resolution transmission electron microscope (HRTEM, JEM-2100F JEOL) equipped with energy dispersed spectroscopy (EDS, INCA Energy 300 mics/x-stream Oxford Instruments). The chemical state was examined by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi ThermoFisher Scientific) spectra. Nano-Measurer was used to analyze the size distribution of the WC particles based on SEM morphology. The elemental content of samples was examined by Inductively Coupled Plasma (ICP, AES OPTIMA 5300DV PE) component test.

3. Results

The SEM image of W powders and W-As composite raw powders is shown in Fig. 1. Our previous research showed that arsenic (As) could refine tungsten powders significantly when adding the quality percentage of arsenic is one percent. The Fig. 1a shows that tungsten powder without doping arsenic is nearly spherical in shape. The Fig. 1b shows that one percent arsenic doped tungsten composite powders appear elaboration phenomenon in general. The SEM images showed that we can obtained good uniformity and dispersion of nanometer tungsten composite powders. As shown in Fig. 1c, the average size of powders is about 80 nm in diameter.

In order to analysis the effect of arsenic on the reaction of powders systems during the carbonization process, Fig. 2 shows the DSC traces of the carbonization reaction of pure W (black lines) and W-As composite powder (red lines) with carbon or glucose as C source, respectively. As shown in Fig. 2a, two endothermic peaks of black line were at 832.9 °C and 971.1 °C, corresponding to the formation of W_2C and WC [19]. The initial and final temperature of the pure W carbonization reaction was 936 °C and 992 °C.

Comparing with the black and red line, the temperature of the second endothermic peak was different. WC-As powders were carbonated at 1063.8 °C which is higher than the pure WC powders. And the initial and final temperature of carbonization reaction was 1054 °C and 1079 °C, respectively. It was obvious that the initial carbonization temperature of the W-As samples was increased 118 °C than that of pure W sample. It was shown that arsenic could delay the carbonization process effectively. Furthermore, the peak of the As-doped samples was sharper which illustrated that the carbonization reaction of the As-doped samples was accelerated. This might be ascribed to that the tungsten particle size decreased after adding arsenic. The nano tungsten powder obviously increased short-circuits diffusion channels and accelerated the speed of diffusion. In this way, carbon atoms can fully contact with tungsten powders effectively and promote the process of carbonization.

Fig. 2b shows DSC traces of carbonization reaction of W-As powder (the red line) and pure W powder (the black line) with

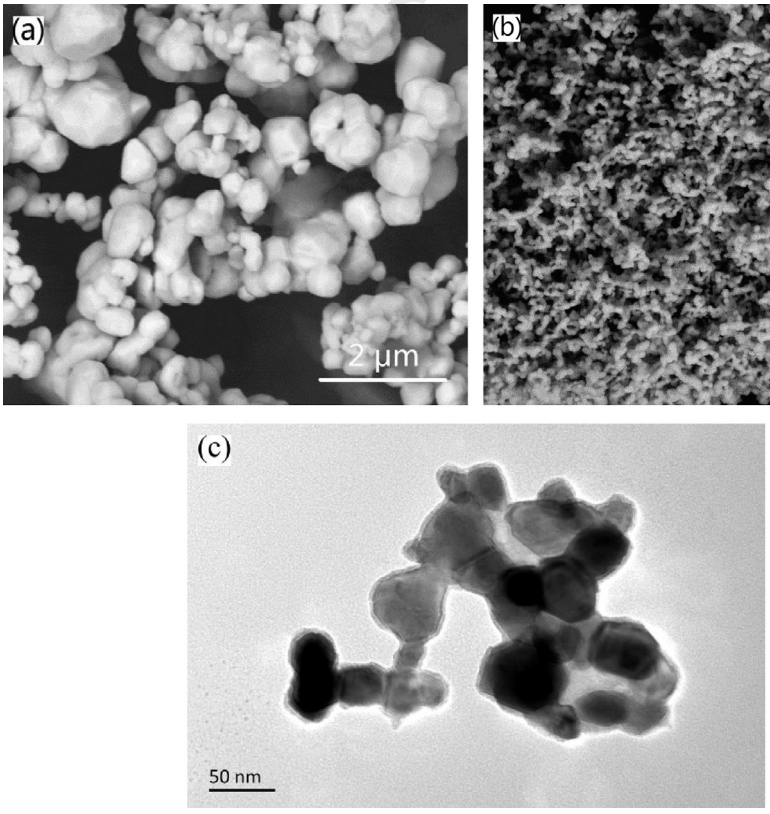

Fig. 1. SEM image of W powders (a) and SEM (b), TEM (c) images of W-As raw powders.

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