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Synthesis of TaC nanopowders by liquid precursor route

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ABSTRACT

TaC nanopowders were synthesized by a liquid precursor route. The synthesis procedures include (1) preparation of tantalum ethylate solution by sufficient mixing $TaCl_5$ powders with ethanol, (2) adding activated carbon nanopowders to the solution, (3) dispersing activated carbon nanopowders in the solution evenly to form a liquid precursor by an ultrasonic equipment, (4) brushing the liquid precursor on an alumina crucible and blowing the liquid precursor to dry, (5) heat treatment in a graphitization furnace in a vacuum, and (6) brushing the alumina crucible to obtain products. X-ray diffraction patterns indicated that the products were cubic TaC. The formation temperature (1300 °C) of TaC in this process is lower than that (1700 °C) in the conventional method. The reaction time of forming TaC in this process is half an hour. The observed size of TaC powders by TEM was smaller than 50 nm. The specific surface area of the powders by a surface area analyzer was 28.399 m^2/g.

1. Introduction

Tantalum carbide (TaC) is frequently referred to as refractory materials and finding applications as cutting tools [1], wear-resistant parts [2] and high-temperature structural materials due to its high hardness, extremely high melting point and excellent high-temperature strength. TaC needed for these applications are conventionally prepared by solid-state reactions of tantalum or tantalum oxide powders with graphite or amorphous carbon at a temperature about 1700 °C leading to powders of a low specific surface area [3–5]. In addition to the classical applications, TaC is being used increasingly for their electrical conductivity and chemical corrosion resistance as electrodes, catalysts [6], conducting films or oxidation-resistant coatings [7]; however, usage in catalysis and electrochemistry requires materials of high surface areas.

Interest in electrical, catalytical and anticorrosion applications has necessitated the development of new preparation techniques. Recently, various preparation techniques have been developed for preparing fine TaC powders with high surface areas. H. Preiss et al. [8] prepared TaC powders with a size less than 1 μm from gel-derived precursors. Dae-Hwan Kwon et al. [9] synthesized ultrafine TaC powders by mechano-chemical process. Takamasa Ishigaki et al. [10] produced TaC nanopowders by injecting a liquid precursor into RF induction plasma. Jianhua Ma et al. [11] reported a new method to synthesize nanocrystalline TaC via the reaction of tantalum pentachloride and sodium carbonate with metallic magnesium.

In this paper, we have investigated a new method to synthesize TaC nanopowders from a liquid precursor. The liquid precursor is a mixture of tantalum ethylate and activated carbon nanopowders prepared by an ultrasonic equipment.

2. Experimental

Preparation of tantalum ethylate solution was made through mixing 0.50 g $TaCl_5$ powders with 5.0 ml ethanol [12]. After sufficient mixing, 0.10 g activated carbon nanopowders (24 nm) was added to the solution. After sufficient mixing, the solution was put in the ultrasonic equipment. In order to disperse activated carbon nanopowders in the solution evenly to form the liquid precursor, the ultrasonic equipment operated at a frequency of 40 KHz, with an output power of 80 W, in a temperature of 55 °C, for 20 min. Then all of liquid precursor was brushed on the surface of an alumina crucible to form a film which was slowly blown to dry. The crucible with the film was put into the graphitization furnace in a vacuum about 100 Pa, and then was heat-treated at 1300 °C for 0.5 h to produce TaC powders. The heating rate was 10 °C/min. At last, the crucible was cooled naturally to room temperature in the furnace and golden-and-black powders were found after brushing the crucible.

The obtained powders were analyzed by X-ray diffraction on a Rigaku D/max-RB X-ray diffractometer. The morphology of the powders was examined on a ZEISS SUPRA 55 field-emission scanning electron microscope and a JEM-2100 transmission electron microscope. The specific surface area of the powders was analyzed on a QUANTASORB-18 surface area analyzer.

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3. Results and discussion

Fig. 1 shows the XRD patterns of the powders prepared under different conditions. As shown in Fig. 1(a), the powders prepared at 1000 °C for 0.5 h consist of Ta_2O_5. The phase assignment is done according to the PDF # 25-0922 for Ta_2O_5. The 5 main peaks for (1 11 0), (0 0 1), (1 11 1), (2 0 0) and (1 11 2) reflections originate at the 2θ values 28.290, 22.902, 36.665, 28.794 and 55.476. There is no peak corresponding to carbon in Fig. 1(a) but the EDS shows the powders containing carbon in Fig. 2(d). Two factors may cause that phenomenon. Firstly, the activated carbon nanopowders are amorphous. Secondly, it is difficult to detect the nano-sized carbon powders which were sufficiently mixed with Ta_2O_5 by XRD.

Fig. 1(d) shows the XRD patterns of the powders prepared at 1300 °C for 0.5 h. It indicates that the powders consist of TaC. The phase assignment is done according to the PDF # 65-0282 for TaC. The 5 main peaks for (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) reflections originate at the 2θ values 34.812, 40.415, 58.483, 69.893 and 73.494. There are no peaks corresponding to tantalum, tantalum oxide, and Ta_2C. The powders prepared at 1100 °C and 1200 °C for 0.5 h both consist of TaC and Ta_2O_5 as shown in Fig. 1(b) and (c). As can be seen in Fig. 1, the proportion of the TaC phase increases with the increasing temperature, contrary to it, the proportion of Ta_2O_5 phase decreases. It indicates that Ta_2O_5 was transformed into TaC above 1000 °C. The TaC was formed completely at 1300 °C, which is lower than the fabrication temperature (1700 °C) of TaC in a conventional process [3–5].

Fig. 2 shows the SEM micrographs of the powders prepared under different conditions. Fig. 2(a) shows the SEM micrograph of the dried liquid precursor. The dried liquid precursor consists of tantalum ethylate and activated carbon nanopowders. The particles whose size is smaller than 100 nm are dispersed in a matrix, as shown in Fig. 2(a). It could not transform activated carbon nanopowders into a matrix without heat treatment. Therefore, the matrix is tantalum ethylate and the particles are activated carbon.

The dried liquid precursor on the crucible was heat-treated in the graphitization furnace in a vacuum about 100 Pa to form TaC. According to Hanwei He et al. [12], in the course of formation of TaC, the tantalum ethylate was decomposed and transformed into TaO below 500 °C, then TaO was transformed into Ta_2O_5 above 500 °C. There is no TaO or TaC existing at 1000 °C, as shown in Fig. 1(a). It indicates complete formation of Ta_2O_5 at 1000 °C and no formation of TaC below 1000 °C. Fig. 2(b) shows the SEM micrograph of the powders prepared at 1000 °C for 0.5 h. The agglomerated particles are rounded and irregular in shape. The average particle size in Fig. 2(b) is found to be below 100 nm. The EDS data on the powders prepared at 1000 °C for 0.5 h indicate that only elements Ta, C and O are detected, as shown in Fig. 2(d). There are no sharp peaks corresponding to carbon in Fig. 1(a) because the activated carbon is amorphous. According to Figs. 1(a) and 2(d), we can know that the powders shown in Fig. 2(b) are consisted of nano-sized Ta2O5 and nano-sized activated carbon.

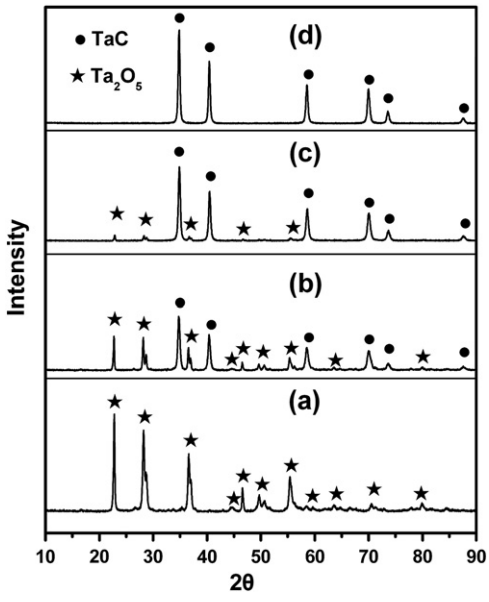

Fig. 1. XRD patterns of the powders prepared under different conditions: (a) 1000 °C, 0.5 h; (b) 1100 °C, 0.5 h; (c) 1200 °C, 0.5 h; and (d) 1300 °C, 0.5 h.

Ta_2O_5 was transformed into TaC above 1000 °C. The overall reaction governing the formation of TaC is $Ta_2O_5(s) + 7C(s) \rightarrow 2TaC(s) + 5CO(g)$ [8]. As the sizes of carbon and tantalum oxide decrease, the reactivity of the formation process described above will increase because of the high specific area of reactants. Therefore, nano-sized Ta_2O_5 mixed with nano-sized activated carbon has so high reactivity that it needs a low temperature and a short reaction time to form TaC. According to the reaction equation, it indicates that the added activated carbon is excess. Fig. 2(c) shows the SEM micrograph of the powders prepared at 1300 °C for 0.5 h. The sizes of agglomerated particles with rounded and irregular shapes are below 100 nm but not uniform. The powders prepared at 1300 °C for 0.5 h consist of TaC and little excess activated carbon which cannot be detected by XRD.

After dispersion by the ultrasonic equipment, the dispersed TaC particles placed on the copper net were observed by TEM, shown in Fig. 3. There are three kinds of particles marked A, B and C in Fig. 3(a). Their EDS are shown in Fig. 3(c–e). The presence of the Cu peak is caused by usage of copper net. The atomic ratio of particles marked A is 85.23%C, 1.99%Ta and 12.78%Cu, indicated by Fig. 3(c). Therefore, the transparent grey particles marked A are activated carbon. Due to carbon's weak electron scattering, the electron can transmit the particles easily to form transparent grey particles. Fig. 3(d) indicates that the atomic ratio of particles marked B is 38.17%C, 33.06%Ta and 28.77%Cu. Therefore, the opaque grey particles marked B are TaC. The electron is difficult to transmit the particles because of tantalum's high electron scattering, so the particles are opaque. The atomic ratio of particles marked C is 39.66%C, 36.26%Ta and 24.08%Cu, indicated by Fig. 3(e). Therefore, the opaque black particles marked C are TaC, too. The black image may be caused by the thickness of the particles. The particles marked C are thicker than the particles marked B. The agglomeration of TaC particles may cause that. The sizes of separated TaC particles are below 50 nm as shown in Fig. 3(a). The sizes of agglomerated TaC particles are difficult to figure out in Fig. 3(a). Fig. 3(b) shows that all of the agglomerated TaC particles sizes are below 50 nm. Therefore, the observed size of TaC powders by TEM was smaller than 50 nm. The specific surface area of the TaC composite powders prepared at 1300 °C for 0.5 h was 28.399 m^2/g.

4. Conclusions

In summary, tantalum carbide (TaC) nanopowders had been successfully synthesized by a liquid precursor route. The liquid precursor was a mixture of tantalum ethylate and activated carbon nanopowders prepared by an ultrasonic equipment. The products had the cubic TaC structure. It consisted of particles with an average size less than 50 nm. The specific surface area of the powders was 28.399 m^2/g. The complete formation of TaC nanopowders could be accomplished by heat treatment at 1300 °C for 0.5 h.

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