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ARTICLE

Effect of Carbon Content on Morphology, Size and Phase of Submicron Tungsten Carbide Powders by Salt-assisted Combustion Synthesis

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Abstract: The diluent NaCl was introduced into the WO_3-Mg-C-Na_2CO_3 system to prepare submicron tungsten carbide (WC) powders via salt-assisted combustion synthesis. The products were analyzed by SEM, EDS and XRD, and the effects of C content on morphology, average particle size and phase composition of the products were studied. Results show that on basis of the m = 0.125 (the number of moles of Na_2CO_3), when the number of moles of carbon in raw material increases from l=2 to 2.25 and 2.5, before leaching, the product is made up of a small number of large size particles and a large number of small size particles; after leaching, samples are composed of aggregates of submicron particles, and the sintering phenomenon between particles is very weak, indicating low degree of aggregation. Particle size distribution of leached product almost falls into the normal distribution, and the particle sizes range from 200 nm to 350 nm. Under the condition of l=2.25, a main target product is WC, and the content of by-products W_2C is extremely few. That is, k = 2.0 (the number of moles of NaCl), m = 0.125, and l=2.25 are the process conditions for single-phase WC synthesis.

Key words: carbon content; salt-assisted combustion synthesis; tungsten carbide powders; morphology; phase

WC has excellent performances such as high melting point, high hardness, low friction coefficient, high oxidation resistance and good electrical conductivity [1]. As carbide with high elastic modulus and high hardness, WC powder is the main component to make cemented carbide. WC-based cemented carbide is mainly applied in many fields such as cutting tools, dies, mining tools and wear-resistant parts [2].

WC is also widely used in the catalyst area [3]. Since Gaziew et al [4] found that WC could catalyze dehydrogenation reaction of cyclohexane in 1961, the research and development of WC has opened up a new field. Then, WC with high catalytic activity was synthesized, and had great catalytic activity in the anodic oxidation reaction of hydrogen.

Nano-WC powder can replace traditional catalysts such as Pt, Pd and Ir. The chemical stability of nano-WC powder is good, and its property of anti-poisoning is better than that of noble metal such as Pt. At present, a lot of researches in this field have been conducted, such as the preparation of WC catalyst, physical and chemical properties, surface structure, and catalytic activity. The research have found that WC catalyst not only can be applied as hydrogen anode in acidic fuel cell and the active cathode in electrolysis, but also can show relatively high activity in catalyzing chemical reactions such as hydrogenation and dehydrogenation.

Due to economic and technical constraints, the quality of the WC applied in high-tech must be high. However, the traditional synthesis methods cannot meet the needs of quality and quantity, so the exploration of new technologies to produce such sort of WC is imperative [4].

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There are many methods to synthesize WC powder such as direct carbonization of tungsten powder, solid state replacement, carbonization reduction, mechanical grinding and using precursor of metal alkoxide polymer [4-8]. Among them the direct carbonization of tungsten powder is the most common method. However, its cost is high, and pure tungsten powder is needed; it is time-consuming and the performance of WC powder produced is not so good.

WC can also be obtained through tungsten carbonization at a relatively low temperature in the atmosphere of CH_4-H_2[9,10]. Although mass production of WC can be conducted by the method, a large amount of free carbon is deposited and W_2C is produced. Besides, the tungsten powder used as the raw materials should be very pure and fine. WC with high quality prepared by this method is not reasonable economically.

Recently, using graphite as the carbon source, WC has been successfully prepared by grinding the mixture of WO_3-Mg and graphite to make them react [11-13]. The method is easy but dangerous, because explosion may happen upon W and Mg reaction.

Direct carbonization of WO_3 by graphite via a mechanical activation method was proposed to prepare WC [14]. Compared with previous methods, the reaction temperature of this method is low and the time consumed is less.

In the present paper, 2 mol of diluents NaCl was introduced into the WO_3-Mg-C system, and at the same time, 0.125 mol (m= 0.125 mol) of Na_2CO_3 and 2 mol (l=2 mol) of carbon were added. The product with the main phase of W_2C was obtained by salt-assisted combustion synthesis, among which the content of WC was relatively less with the average particle size of 327 nm. On this basis, the mole number l of carbon increased from 2.25 to 2.5 and finally single phase WC was obtained when l was 2.25 with the average particle size of 301 nm.

1 Experiment

Raw materials included: WO_3 (purity> 99%), Mg powder (purity> 99%), C (purity> 99%), Na_2CO_3 (purity> 99.8%), and NaCl (purity> 99.5%). The system chosen to prepare WC powder by combustion synthesis was WO_3-Mg-C. The related W carbonization reaction was a solid phase reaction, that is, $2W+C\rightarrow W_2C\rightarrow WC$. NaCl was introduced into the experimental materials to provide a liquid reaction medium. At the same time, Na_2CO_3 was added to improve the gas transfer in the reaction to facilitate carbonization process to obtain the single phase product. On the basis of experiment, the effect of the carbon content in the raw materials was studied. The constituent of raw materials was as follows:

$$l\mathrm{C} + 2.5\mathrm{Mg} + \mathrm{WO_3} + 2\mathrm{NaCl} + 0.125\mathrm{Na_2CO_3} \quad (1)$$

where the values of l were 2.0, 2.25 and 2.5, that is, the content of C increased gradually. The C content in the raw materials was excessive to some extent.

The reactant powders were weighed. The reactant powders and alumina grinding balls were manually pre-mixed in the stainless steel ball mill with the mass ratio of 2:1. The reactant powder and grinding ball were completely mixed in the planetary ball mill after sealing the ball mill. The rotation speed was 150 r/min. The planetary ball mill was stopped every 10 min. Rotation was reversed again. The reactant powders were evenly mixed and then placed in the die; Round samples with the diameter of 20 mm and the height of 10 mm were prepared on the press at the pressure of 15 MPa.

The reaction was carried out in a combustion synthesis reactor made by China. Firstly, the ignition agent tablets was placed in the copper crucible of the reactor. Then, the round sample was placed on the tablets. Afterward the reactor was sealed and heated. 0.5 MPa argon was filled and held for 10 min. The gas was purged to remove air in the reactor. When the temperature in the reactor rose to 180 ºC, 2 MPa argon was filled again. When the temperature of the reactor rose to about 250 ºC, the ignition agents reacted and released much heat. The samples underwent the self- propagating reaction. The combustion wave spread through the entire sample within tens of seconds. The reactants turned into lumps containing the target product.

The lump product obtained through combustion synthesis contained the target product WC, the reduction product MgO, the remained diluent NaCl and so on. Thus, the lump product needed leaching to remove the impurities. For the purpose the lump product was ground into powder in the grinder. The leaching reaction is listed as formula 2. The leaching agent (HCl of 9.6 mol/L) was excessive 50 wt% of the stoichiometric ratio. The leaching reaction lasted 3 d. The leaching liquid was stirred 3 to 5 times every day. WC existing in the leaching liquid in solid state was separated by pumping filtration, and remained in the Buchner funnel. Then distilled water was added into the funnel. WC was washed 5 times to remove the remained hydrochloric acid in the target product. The powder obtained by separation was taken out and placed in the vacuum oven of 100 ºC to be dried for 12 h. The final WC powder was obtained.

$$2\mathrm{HCl} + \mathrm{MgO} = \mathrm{MgCl_2} + \mathrm{H_2O} \quad (2)$$

2 Results and Discussion

2.1 Morphologies of the product with different carbon content

To obtain single-phase WC, the carbon content in the raw materials should be increased to make more intermediate W_2C, which will be further carbonized to generate target product WC. On the basis of m = 0.125, the mole number of carbon in raw materials increased from 2.25 and 2.5. Fig.1 shows the microscopic morphologies of the product obtained through combustion synthesis, when l = 2.25, 2.5. The products consist of large size particles and a large amount of small size particles. The EDS of the sample shows that the