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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].

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:

$$lC + 2.5Mg + WO_3 + 2NaCl + 0.125Na_2CO_3 \qquad (1)$$
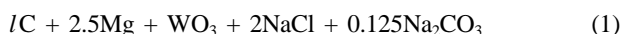
where the values of l were 2.0, 2.25 and 2.5, that is, the content of C increased gradually. The C content in the raw materials was excessive to some extent.

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 ℃, 2 MPa argon was filled again. When the temperature of the reactor rose to about 250 ℃, 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 ℃ to be dried for 12 h. The final WC powder was obtained.

$$2HCl + MgO = MgCl_2 + H_2O \qquad (2)$$
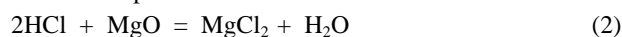
2 Results and Discussion

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

peaks of Mg, Na, O and Cl are relatively strong and the peaks of W and C are relatively weak at large particles. The average mass fraction of Mg, Na, O and Cl is more than 90 wt%, while the average mass fraction of W and C is less than 10 wt%. The components of small size particles is on the contrary, the average mass fraction of W and C is more than 80 wt%, while that of the other four elements is relatively less.

The morphologies of the leached product are shown in Fig.2. Both samples are made up of the aggregates of sub-micron particles. Pores exist inside the aggregates. The sintering phenomenon between particles is very weak, indicating low degree of aggregation. Small size particles are close to sphere or ellipsoid, while large size particles exhibit irregular shape with facets.

Energy spectra analysis was also conducted on the leached product with $l = 2.25$ and the results suggest that the mass fraction of C and W is 97.41 wt% and the remained is O element.

2.2 Average particle size and particle size distribution

The particle size distribution of the leached products is shown in Fig.3. The particle sizes of both samples almost fall into the normal distribution. The particle sizes are between 100 and 650 nm. The average particle sizes of the both samples are almost the same, with the values of 301 and 306 nm.

2.3 Phase of the products with different carbon content

Fig.4 is the XRD patterns of the leached WC products with different carbon contents. It is from the picture, as for the samples with the carbon mole number of $l = 2$, 2.5, the diffraction peaks of byproducts are relatively strong, and the diffraction peaks of the target products WC are relatively weak, suggesting that the byproduct contents obtained under both conditions are relatively high, while the target product contents are relatively low. As for the sample with the carbon mole number of $l = 2.25$, the diffraction peak of the target product WC is very strong, while the diffraction peak of byproduct W_2C is relatively weak, suggesting that under the condition of $l = 2.25$, the synthesized product is mainly the target product WC and content of the byproduct W_2C is very low. That is, $k = 2.0$, $m = 0.125$, and $l = 2.25$ are the process conditions of single-phase WC prepared through combustion synthesis in the WO_3-Mg-C system.

2.4 Formation mechanism of ultrafine single-phase WC

In the present work, WC was prepared by the salt-assisted combustion synthesis method in the WO_3-Mg-C system. When the temperature of the reaction reaches the ignition point, the liquid Mg fully contacts with WO_3, and redox reaction occurs to generate intermediate W. The reaction equation is shown as follows:
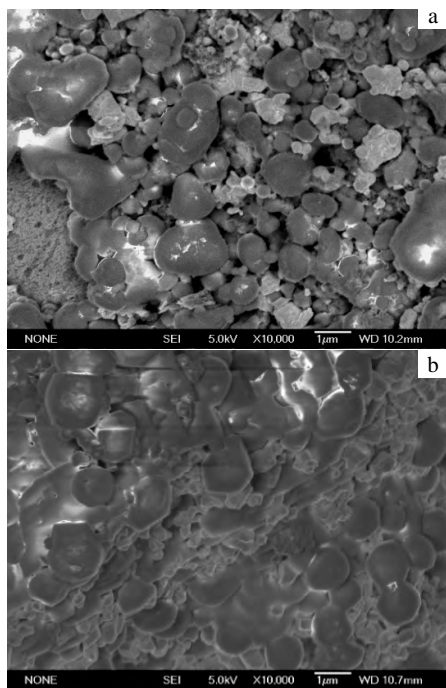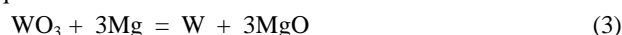
$$WO_3 + 3Mg = W + 3MgO \tag{3}$$

$$W + 2C = W_2C \tag{4}$$

$$W_2C + C = WC \tag{5}$$

Fig.1 SEM images of combustion synthesis products with different carbon contents (before leaching): (a) $l = 2.25$ and (b) $l = 2.5$
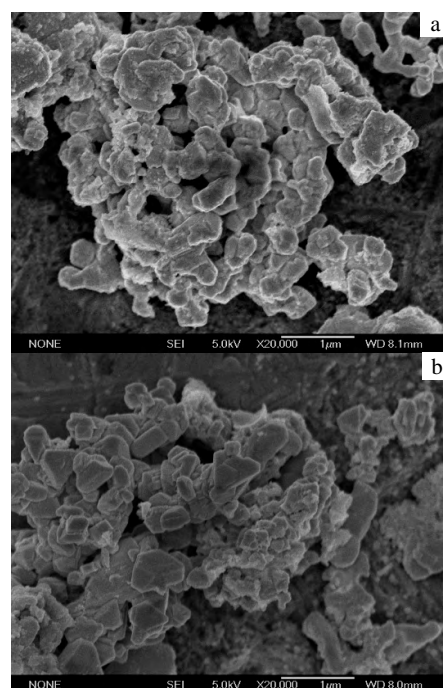

Fig.2 SEM images of combustion synthesis products with different carbon contents (after leaching): (a) $l = 2.25$ and (b) $l = 2.5$
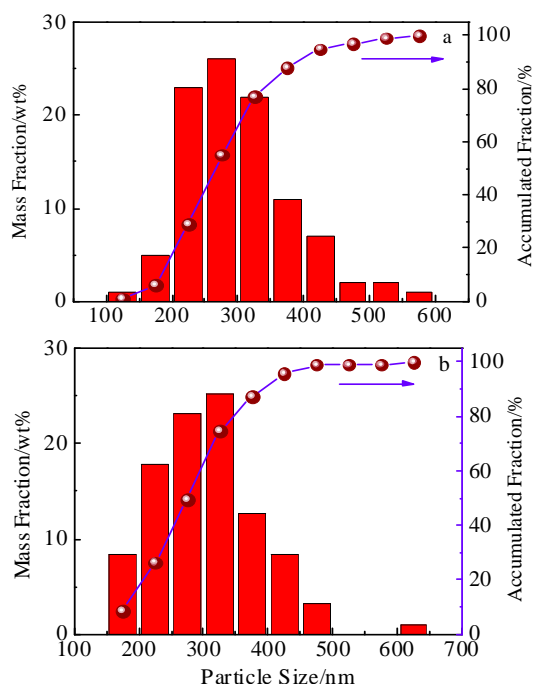
Fig.3   Particle size distribution of combustion synthesis product with different carbon contents (after leaching): (a) $l=2.25$ and (b) $l=2.5$

Fig.4   XRD patterns of leached product with different carbon contents

The process occurs in the liquid medium of NaCl. A large amount of small size W particles are generated as formula 3. On one hand, the surface area of W particles increases to a great extent to make it easier for W particles to seize carbon atoms. On the other hand, the diffuqion path of C atoms to W particles is shortened to create favorable conditions for the carbonization process [15]. At the same time, Na_2CO_3 is added into the reactants. In the combustion process, Na_2CO_3 reacts with WO_3 as the formula 6 to form gas product CO_2. As the carbonization process continues, the C atoms gradually diffuse into the inside of W particles, leading to the lack of C atoms on the particle surface. A proper excess of carbon sources exists in the surrounding. The liquid NaCl and gasous CO_2 can provide liquid phase transmission and gas phase transmission for the diffusion of C atoms, accelerating the supplement of carbon sources on the surface of W particles and finally single phase WC is obtained. It is noteworthy that when the carbon content is excessive, a carbon coat will be formed around the surface of W particles, where the supply of carbon is more than the need of carbonization. However, the diffusion of C atoms inside the coat is very weak. Thus, the practical carbonization process is suppressed or even stopped [16], which is impossible to form single-phase WC.
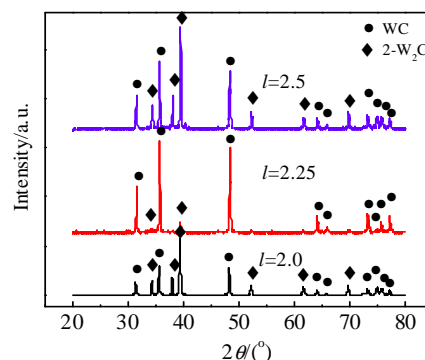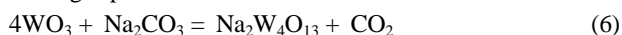
$$4WO_3 + Na_2CO_3 = Na_2W_4O_{13} + CO_2 \qquad (6)$$

In addition, in the carbonization process of W particles, with continual diffusing of C atoms into their inside, W gradually turns into W_2C, and at the same time, W_2C turns into WC. With the gradual disappearance of W and W_2C, the entire particle will expand, and split into multiple WC particles. With the formation of a large number of WC particles, WC becomes saturated in NaCl and then precipitates in the melt. Thus, the relative small size formed by carbonization can be maintained. However, it is difficult for the WC particles to exist inside the melt to recrystallize and grow after the solidification of NaCl and finally small size particles can be formed.

In summary, success of single-phase WC by combustion synthesis needs three requirements: (1) proper sufficient carbon is supplied; (2) the effective diffusion of C atoms into the particles inside is guaranteed; (3) small size W particles are formed.

3 Conclusions

On the basis of the WO_3-2C-2.5Mg-2NaCl-0.125Na_2CO_3 system, the C content increases further, and when the mole number of C is 2.25, the product is mainly WC with the mass fraction of about 97.41% and the average particle size of 301 nm. When the mole number of C increases to 2.5, the product is also mainly W_2C

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WC

1　　　　2　　　1　　　　1　　　2　　　2

(1.　　　　　　　　　　　　　　　　　　　　　　　　730050)

(2.　　　　　　　　　　　　730050)

WO$_3$-Mg-C-Na$_2$CO$_3$　　　NaCl　　　　　　　　　WC　　　　　SEM

EDS　　X　　　XRD　　　　　　　　C　　　　WC

$m=0.125$　Na$_2$CO$_3$　　　　　　　　　　　$l=2$　　2.25　2.5

200~350 nm　　　$l=2.25$　　　　　　　　WC　　　W$_2$C　　　$k=2.0$　NaCl

$m=0.125$　$l=2.25$　　　WC

C　　　　　WC

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