Development of Fine-Grain Tungsten Carbide Powder Using a Chemical Solution Process

液相プロセスを用いた炭化タングステン微粉末の開発

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Abstract

We prepared high purity, fine tungsten carbide powder using a chemical solution composed of tungstic acid, citric acid and ammonia solution. Precursor powder, obtained by spray-drying the chemical solution, was heated under argon to 1423 K. Total carbon of the heat-treated precursors was controlled by adjusting the molar ratio of citric acid and tungstic acid. The carbonization temperature was lower than conventional methods using carbon and tungsten trioxide or tungsten, therefore grain growth was suppressed. The grain size of obtained tungsten carbide was approximately 100 nm. Impurities (iron and cobalt) were less than 10 ppm.

タングステン酸、クエン酸、アンモニア水溶液を用いた液相合成により高純度かつ微細な炭化タングステン（WC）粒子を合成した。錯体溶液を乾燥して得た前駆体粉末は 1423K、アルゴン雰囲気中で熱処理された。前駆体粉末を熱処理して得られた粉末中のトータルカーボン量はクエン酸とタングステン酸のモル比により調整
1. Introduction

In cemented carbides predominantly composed of tungsten carbide (WC), hardness is improved by decreasing crystal grain size and strength is improved by decreasing impurities such as iron (Fe). Therefore, the fine and pure WC powder is required for optimal hardness and strength. Much research has been reported on the reduction and carbonization process using tungsten (W) or tungsten trioxide (WO3) and carbon (C) mixed powder. The factors affecting grain growth in the process of WC formation have been reported. Grain growth of W is avoidable because it occurs at a lower temperature than the carbonization reaction temperature. Thus, the direct carbonization method using WO3 and C mixed powder is effective [1]. 80-nm WC powder is obtained by a two-step heating process. In the primary heating process, under nitrogen, WO3 and C mixed powder reacts to give W and ditungsten carbide (W2C). In the secondary heating process, under hydrogen, the intermediate powder is heated to 1373 K. And it was indicated that WC powder grew up in case of tungsten oxides were remained during secondary heating process after primary heating process [2]. Moreover, under hydrogen, water vapor caused W grain growth when heating W oxides [3-4].

In the conventional solution process for manufacturing fine carbide powders, high-molecular-weight organic compounds such as phenol are used as the C source because of their high remaining C. However, these compounds dissolve in only organic solvents, so materials that can be used as a W source are limited and expensive, such as tungsten ethoxide or tungsten carbonyl compounds.

Low cost W materials for manufacturing WC powder include tungstic acid or ammonium paratungstate, which are obtained as intermediate products in conventional WC powder purification processes. These materials are water soluble, so water soluble organic compounds must be used as a C source. Generally, water-soluble low-molecular-weight organic compounds are unsuitable as a C source owing to high numbers of oxygen atoms in their structure. However, in the present study, we attempted to synthesize 100-nm WC powder using a simple process. We used a low-cost precursor solution composed of tungstic acid (H2WO4), citric acid (C6H8O7) and ammonium hydroxide (NH4OH).

2. Experimental

The manufacturing process is shown in Fig. 1. Precursor solutions were prepared using a certain percentage of tungstic acid added to a given concentration of ammonia solution, stirred to dissolve, then added to certain percentage of citric acid and stirred to dissolve. Here, the C/W molar ratio (the ratio of citric acid to tungstic acid) was controlled to between 0.95 and 1.2. The precursor solution was then spray-dried to obtain the precursor powder. The precursor powder was heated under argon to 1173–1673 K in a C crucible.

WC powder obtained using this method was analyzed qualitatively by X-ray diffraction and the morphology was observation by scanning electron microscopy. Total C was measured by combustion infrared absorption equipment, and Fe and cobalt (Co) impurities were measured by inductively coupled plasma atomic emission spectrophotometry equipment.
3. Results and Discussion

3-1. Selection of tungstic acid and citric acid composition

In the present study, an ammonia solution was included to improve the solubility of tungstic acid, and to balance the charge as a cationic component because tungstic acid and citric acid are anionic components. To optimize synthesis conditions, the stable precursor powder was obtained without separating out tungstic acid and citric acid and precipitating.

Total C in the precursor powder is shown in Fig. 2. The C/W molar ratio refers to ratio of citric acid and tungstic acid. The C content of the precursor powder increased with increasing C/W molar ratio, so citric acid was added as raw C source material was combined in the precursor.

Total C in the WC powder is shown in Fig. 3. The C/W molar ratio is controlled by optimizing the compounding ratio of the raw materials. Total C in the WC powder was 6.10–6.15 wt.% under C/W molar ratio controlled between 1.0 and 1.05. When the molar ratio is less than 1.0, the C source is insufficient, and there is an increase...
in the amount of metal carbide containing little free metal or combined C. In contrast, when the molar ratio is more than 1.05, available C is excessive and free C is formed. Thus, both cases result in a reduction in the purity of the fine metal carbide particles.

3-2. Selection of heat-treatment temperature

X-ray diffraction patterns of powders prepared under each heat-treatment temperature are shown in Fig. 4. Scanning electron microscopy images are shown in Fig. 5. The C/W molar ratios of these powders were 1.0. As shown in Fig. 4, powder heated to 1173 K consisted of metal W and unreacted WO₂ and C. Powder heated to 1423 K and 1673 K consisted of only WC with no W or unreacted W oxides. As shown in Fig. 5, in powder heated to 1173 K, grain size was fine but included unreacted substance. In powder heated to 1623 K, grain size was coarse because of grain growth. In powder heated to 1473 K, grain size was fine and included no unreacted substances. Thus, the optimal heat-treatment temperature was selected as 1423 K. Powder obtained using the optimized process consisted of only WC without W or W₂C, and the average grain size was approximately 100 nm. The total C was 6.10–6.15 wt%. The mixing ratio of raw materials was very important for controlling total C in WC powder.

![Fig. 4 X-ray diffraction patterns of tungsten carbide powder heat treated at (a) 1173 K, (b) 1423 K and (c) 1673 K](image-url)
Fig. 5 Scanning electron microscopy images of the tungsten carbide powder heat treated at (a) 1173 K, (b) 1423 K and (c) 1673 K.

The formation reaction of WC particles in this process was considered. In this method, an approximately stoichiometric composition of WC was formed from excess C in the precursor. The weight ratio of C atoms for W atoms was equal, that is, the molar ratio of C atoms for W atoms was 6 to 1. The producer gas during heat-treatment consisted of carbon monoxide (CO), carbon dioxide (CO₂), water (H₂O), ammonia (NH₃), and other organic gases, as analyzed by mass spectrometry. It was considered that excess C atoms for W atoms, and oxygen atoms for C atoms in precursor powders, were removed as CO, CO₂, and other gases in the argon gas flow, leaving only combined C. Impurities such as Fe and Co were 10 ppm or less measured by inductively coupled plasma atomic emission spectrophotometry equipment. Although this manufacturing process didn’t include hard mechanical pulverizing process, extremely pure and fine powder was obtained.

4. Conclusion

Fine grain size WC powder (about 100 nm) was prepared using a simple process. In this process, the precursor was synthesized by from tungstic acid, citric acid and an ammonia solution. This precursor solution was spray dried to obtain the precursor powder. Under argon, the precursor powder was then heated to 1473 K. Extremely pure WC powder with no free C or impurities was obtained by optimizing the ratios of the raw materials and the manufacturing condition.

References