Research paper

Synthesis of tungsten carbide through wire explosion of tungsten in liquid paraffin

Shigeru Tanaka*†, Naoki Kawaji*, Naoyuki Wada*, and Kazuyuki Hokamoto*

*Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto City, Kumamoto 860-8555, JAPAN
Phone : +81-96-342-3902
†Corresponding author : tanaka@tech.eng.kumamoto-u.ac.jp

Received : March 13, 2013 Accepted : December 26, 2013

Abstract

The synthesis of tungsten carbide was conducted by the wire explosion of tungsten under an intense electrical current in liquid paraffin, and ultrafine tungsten carbide powder in the order of nm was successfully recovered. X-ray diffraction analysis results revealed the recovered powder was extremely strained cubic WC_{1-x}. TEM observations confirmed the presence of many twinned regions in each cubic WC_{1-x} particle. In addition, a unique core-shell structure was observed where WC_{1-x} particles were covered by a copper layer.

Keywords : tungsten carbide, wire explosion, high-capacity condenser bank, liquid paraffin, core-shell structure

1. Introduction

Tungsten carbide (WC) can be used over a wide range of temperatures owing to its unique properties including high melting point (2900 °C), high hardness (HV = 1800-2000), high modulus of elasticity (720 GPa) and good wear resistance[1]. Research in the field of nanometer sized powders (1-100 nm) has recently gained importance in materials science and nanometer sized WC powder is considered as one of the important new fine ceramic materials. WC is widely used for manufacturing cutting tools, metal forming tools, mining tools, and wear resistant surfaces with a wide range of applications. There are a number of processes for the synthesis of WC powders including direct carburization of tungsten powder, solid-state metathesis, reduction-carburization, mechanical milling and polymeric precursor routes using metallic alkoxide and each process produces powders with different characteristics[2)-5)]. The main drawbacks to these methods are high production costs and long processing times. Recently, Jiang and Yatsui[6] have demonstrated that it is possible to produce nanometer sized particles in a cost-effective way by using wire explosion process. They produced nanometer sized WC particles by exploding tungsten conductor in different carburizing mediums namely carbon dioxide and methane gas. In their investigation, the recovery of hexagonal tungsten mono-carbide (WC) production was low for the lack of carbon source[7]. Kwon and co-workers[8] tried wire explosion in carbon rich liquid hydrocarbon, such as Hexane, Decane, Benzen and Toluene, using 0.9 kJ power stored in a high capacity condenser. And they succeeded in efficient synthesis of carbide. Phase composition of the products was W, W_2C and WC_{1-x}. The WC_{1-x} is a non-stoichiometric compound which is bonded as a ratio of 1 : 1 -x. And the number that is smaller than1is substituted into the x. On the other hand, Hokamoto and co-workers[9] successfully synthesized nanometer sized TiN powder using wire explosion process under relatively high energy at 10 kJ. Liquid nitrogen was used to react with the exploded titanium wire by the same wire explosion process. The present paper investigates the possibility of synthesizing tungsten carbide through electric wire explosion of tungsten under a stored energy of 10 kJ in liquid paraffin. Paraffin is known to be harmless for human body and the use of paraffin as a carbon source has never been investigated before because the atomic ratio of carbon is relatively lower than other hydrocarbons.

2. Experimental

The experiments were performed in a steel container as illustrated in Figure 1. The tungsten wire used for this experiment was provided by Niraco Co., Ltd. (99.5 mass % tungsten). The liquid paraffin was provided by Nakarai Tesque Co., Ltd. (0.86-0.88 g ml^{-1}). A high-capacity oil

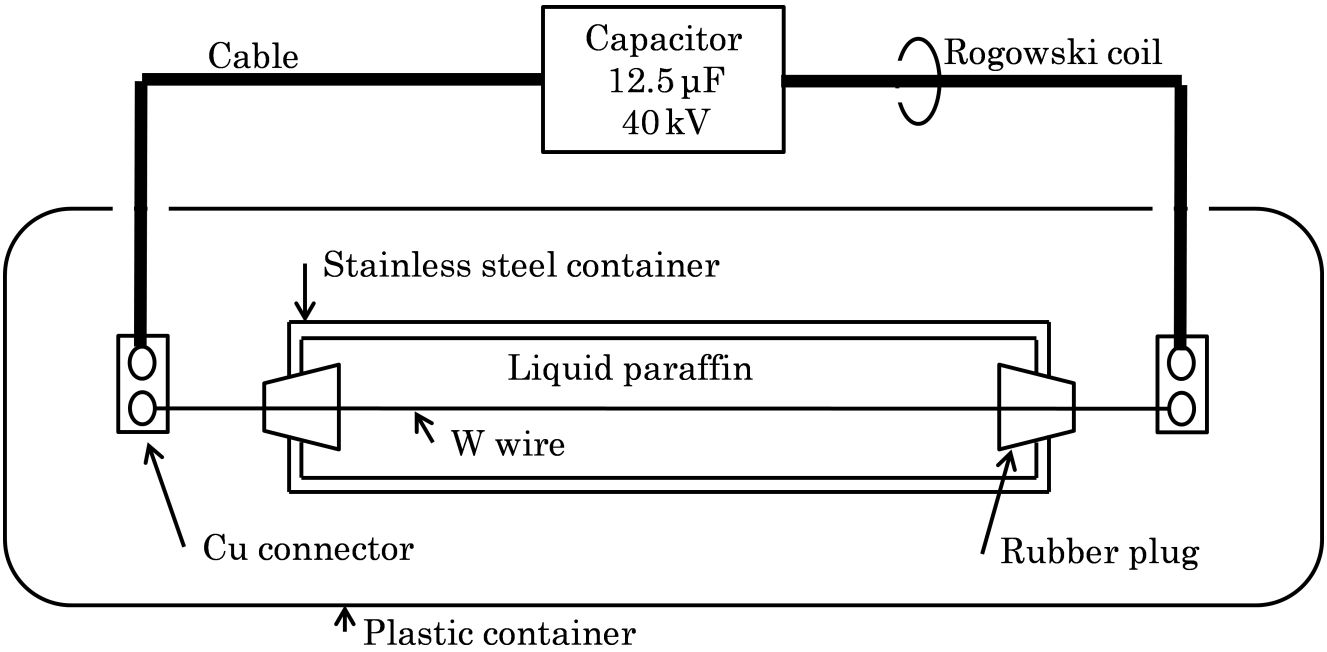


Figure 1 Schematic illustration of assembly used for wire explosion.

condenser capable of storing energy up to 10 kJ (12.5 μF, 40 kV) made by Nichicon Corporation and equipped at Institute of Pulsed Power Science, Kumamoto University was employed for the experiments. The oil condenser is used for the high voltage electricity circuit and the features are high capacitance and non-polar character. In the present work, the experiments were performed at the maximum capacity of the condenser (10 kJ). The length and the diameter of the tungsten wire were 180 mm and 0.5 mm, respectively. The change of current with time was measured using a Rogowski coil attached to the cable. The output voltage from Rogovsky coil is used for the trigger signal of the high-speed video camera too.

For the observation of exploding process in the liquid paraffin, a special vessel was prepared using transparent material (PMMA). Figure 2 shows the images of the explosion process taken by the high-speed video camera (Shimazu Co., Ltd., HPV-1). The input trigger time was defined as 0 μs in Figure 2. A tungsten wire of diameter 0.5 mm, length 180 mm was initially set at horizontal direction in liquid paraffin. From the series of pictures, it can be seen that a plasma emission of the tungsten wire was started from 1 μs. Also, the emission band grew for 5 μs gradually, while the intensity of emission was kept for 7 μs followed by a decrease after 8 μs.

Figure 3 illustrates the waveform shape of discharge current. As can be seen in Figure 3 (point A), an electric current of around 20 kA flowed through the tungsten wire soon after discharge. Phase transition from solid to vapor impeded the current flow (Figure 3 (between point A and B)). In the case that plasma emission was high (Figure 2 (4 to 7 μs)), a large electric current flowed (Figure 3 (ellipsoidal area C)), which was in a good agreement with our observation.

3. Results and discussion

A small amount of powder was recovered from plastic container and it was processed by diethyl ether dissolution treatment, and then, dried at room temperature. X-ray Diffraction (XRD) pattern of the powders reflected the peaks of cubic meta-stable tungsten carbide (γ-WC_{1-x}, Joint Committee for Powder Diffraction Standards (JCPDS) 20-1316) and small amount of tungsten which is shown in Figure 4. It is worth to note that γ-WC_{1-x} is a superconducting material[10] with a cubic crystal structure which is synthesized through quenching of molten condition.

The chemical compositions of both tungsten and carbon were analyzed in the powder using an Inductively Coupled Plasma (ICP) emission spectrophotometer and Infrared absorption method after combustion. As a result, the mass percentage of tungsten and carbon were measure to be 76.0 and 17.5 respectively. However, the peak of carbon was not observed in the x-ray analysis. Therefore, it can be considered the carbon rich phase was induced as mixture of γ-WC_{1-x} and amorphous phase[11]. Furthermore, it is thought that the amorphous carbon is hydrogenated. There is a report that the plasma-assisted Chemical Vapor Deposition (CVD) processes led to hydrogenated amorphous carbon[12]. Because the amorphous carbon is considered as a material in superior with its lubricity, the γ-WC_{1-x} plus amorphous carbon powder may be available as abrasive while the γ-WC_{1-x} alone is a hard material[13].

The quantity of carbon in the WC_{1-x} can be estimated using the following equation[10]. Where a (y) is lattice constant, y is carbon quantity equal to (1-x);

$$a\,(y) = 0.4015 + 0.0481y - 0.0236y^2 \qquad (1)$$

Based on average values of the main five peaks, the lattice constant was 0.4242 nm and of the carbon quantity (y) was 0.734 nm. Hence, it is believed that 3.6 %wt of carbon was combined with tungsten, and 13.8 % of the remaining existed as amorphous carbon.

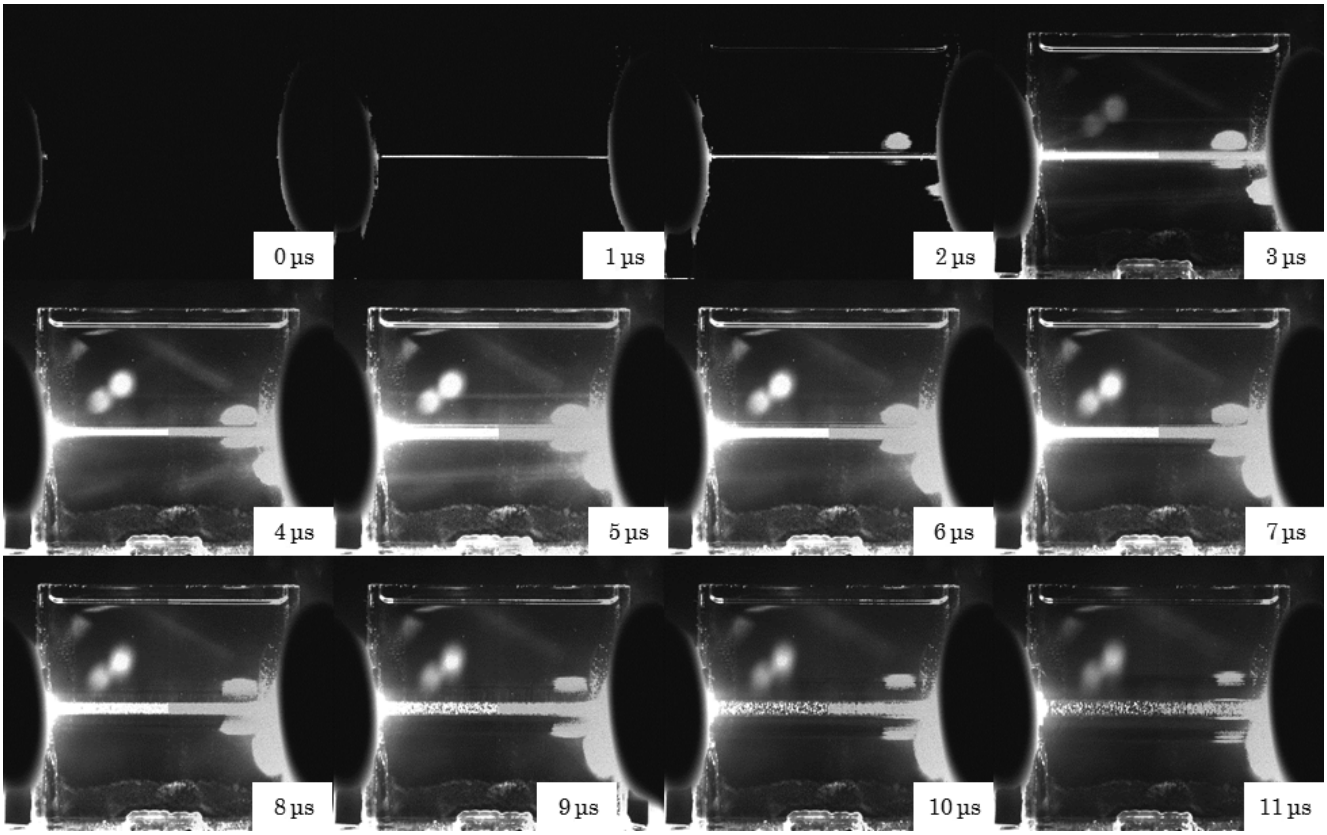


Figure 2 Explosion of the tungsten wire in liquid paraffin during discharge.

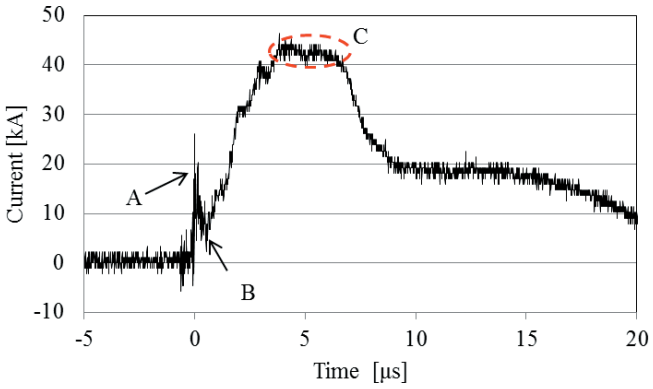


Figure 3 Change in electrical current during explosion.

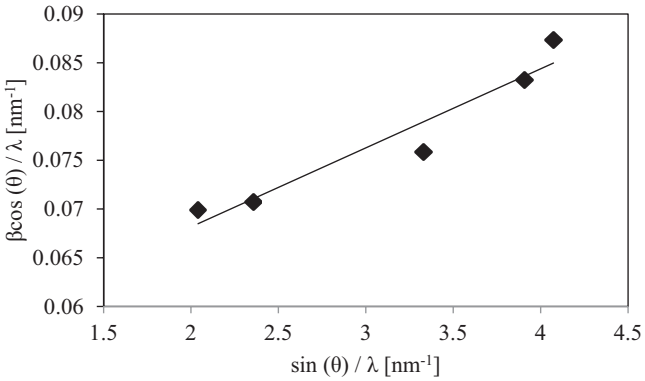


Figure 5 Williamson-Hall plot of recovered γ-WC_{1-x} powder.

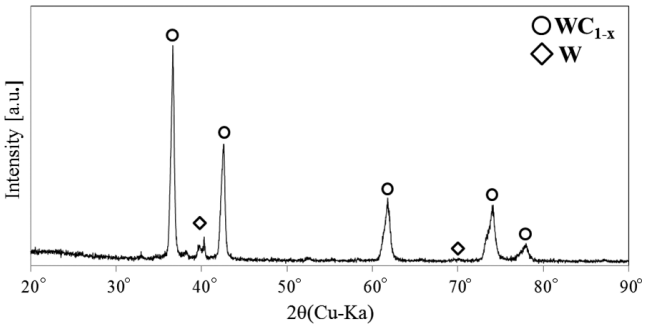


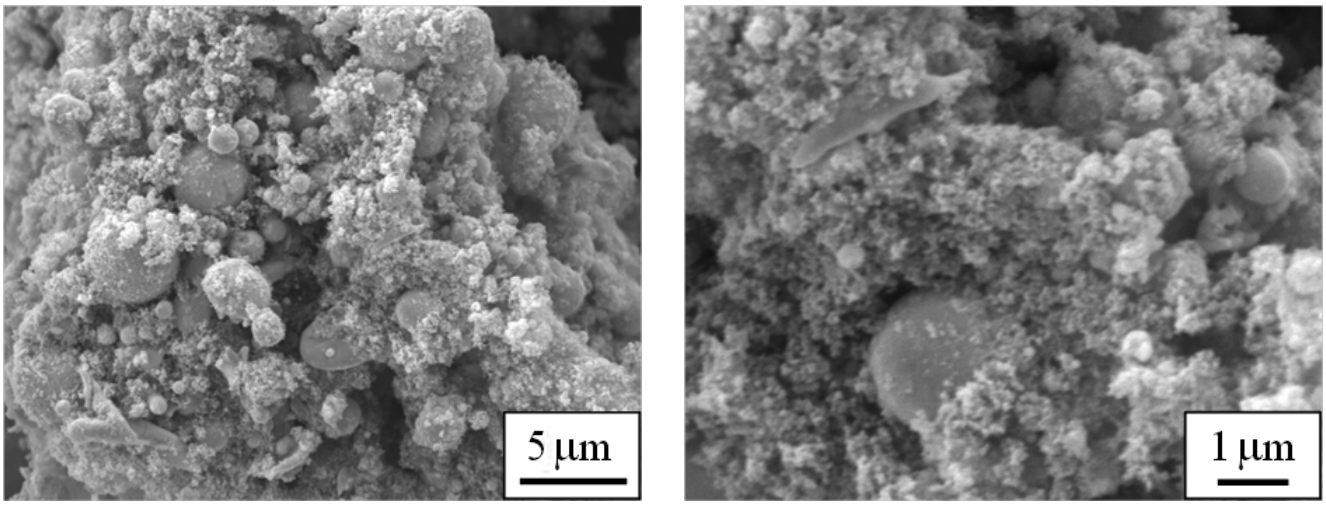
Figure 4 X-ray diffraction pattern for recovered powder.

The Williamson-Hall plot by the x-ray peaks are shown in Figure 5. Parenthesis notation in Figure 5 shows Miiler indices. The plot is drawn using the following equation[13], where β is the half height width of the peaks, λ is the wavelength of the x-ray, ε is crystalline size and η is crystalline strain. All five plots are almost on the straight line.

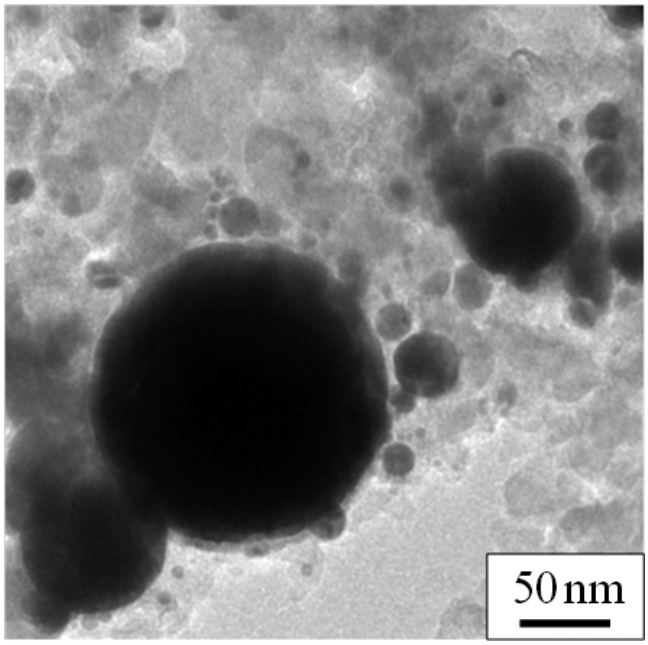
$$\beta \frac{\cos\theta}{\lambda} = 2\eta \frac{\sin\theta}{\lambda} + \frac{1}{\varepsilon} \quad (2)$$

The calculated crystalline size and the strain for the recovered WC_{1-x} particle were 19.3 nm and 0.405 %, respectively. As a result, the WC_{1-x} particle obtained by this process was greatly-strained as suggested for explosively consolidated diamond powders[14].

The Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) images of recovered powder are shown in Figure 6. The aggregates are consisted of nanometer sized particles and relatively large particles as can be seen. The spherical shape indicates that these particles were formed by rapid solidification through liquid phase. Whilst SEM observation failed to reveal the aggregate shape of nanometer sized particles, they looked as spherical shape by TEM observation. The extremely fine spherical



(a) SEM



(b) TEM

Figure 6 Electronic microscope images of recovered powder.

particles less than 10 nm were confirmed. The fringe pattern was confirmed in some particles as shown in Figure 7. The same type of fringe pattern in WC particle has been produced by the wire explosion[7]. Yu et al.[15] reported the fringe pattern in the spherical particle has twinned structure. Figure 8 shows a unique microstructure of a particle covered with a thin layer formed on the core[16]. Figure 8 (b) shows that the layer was composed of layered crystals. Chemical compositions of this particle were analyzed using Energy Dispersive X-ray spectrometry (EDX) attached to TEM. Tungsten and copper peaks were confirmed as shown in Figure 9. At this current research, tungsten wire was connected to copper electrode and the wire was filled with paraffin only at the center position as shown in Figure 1. Therefore, it is considered that the copper and tungsten atoms turned to plasma state by an electrical discharge at the edge part of the assembly. It is believed that at first tungsten particle was formed due to its high melting point, and then the particle trapped copper clusters (liquid) to form a core-shell structure. Creation of such double-layered structure could possibly be considered a unique feature of wire-explosion as well.

4. Conclusion

The tungsten wire explosion using an intense electrical energy enables the synthesis of γ-WC_{1-x} under conditions of the explosion in the liquid paraffin. The γ-WC_{1-x} was strongly strained and composed of amorphous carbon. The particle synthesized had a spherical shape with a twinning structure. Besides, a unique core-shell structure of tungsten covered with a thin layer of copper was also observed in the powder recovered.

Acknowledgement

This research was supported by The Foundation for the Promotion of the Industrial Explosives Technology.

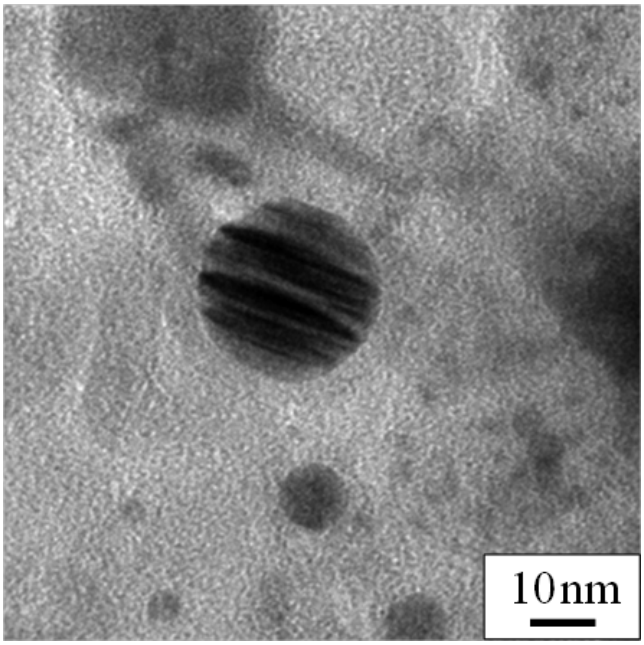


Figure 7 Spherical particle with fringe pattern.

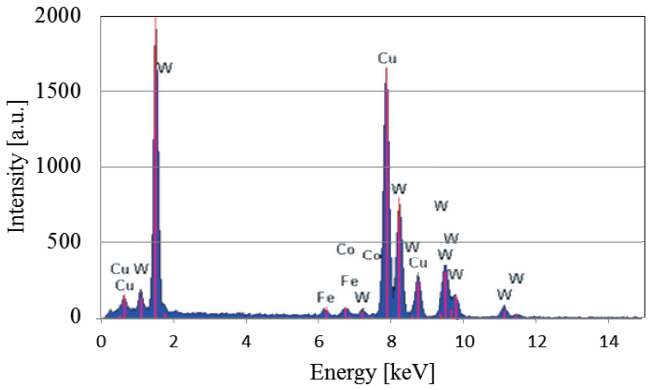
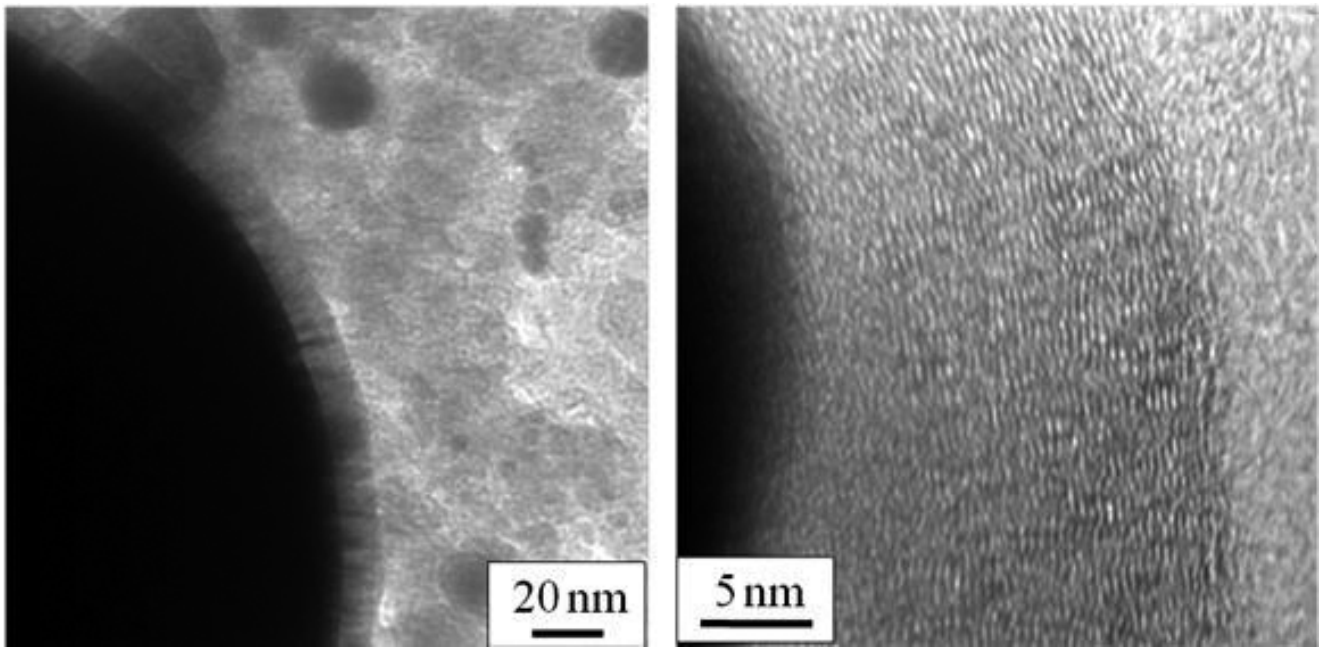


Figure 9 Particle elements analyzed by EDX.

Reference

1) Nihon Kinzoku Gakkai, Kinzoku Data Book, 292 (2004).
2) F. H. Ribeiro, R. A. D.Betta, G. J. Guskey, and M. Boudart, Chem. Mater., 3, 805–812 (1991).
3) R. Koc, S. K. Kodambaka, and J. Eur. Ceram. Soc., 20, 1859–1869 (2000).
4) R. Koc, and S. K. Kodambaka, J. Mater. Sci. Lett., 18, 1469–1471 (1999).
5) F. F. P. Medeiros, S. A. D. Oliveira, C. P. D. Souza, A. G. P. D. Silva, U. U. Gomes, and J. F. D. Souza, Mater. Sci. Eng., A 315, 58–62 (2001).
6) W. Jiang, and K. Yatsui, IEEE Trans. Plasma Sci., 26, 1498–1501 (1998).
7) B. Debalinaa, M. Kamaraja, B. S. Murthya, S. R. Chakravarthic, and R. Sarathib, J. Alloy. Compd., 496, 122–128 (2010).
8) Y. S. Kwon, J. S. Kim, H. T. Kim, H. K. Lee, O. Nazrenko, and A. Ilyin, J. Ind. Eng. Chem., 10, 949–953 (2004).
9) K. Hokamotoa, N. Wada, R. Tomoshige, S. Kai, and Y. Ujimotod, J. Alloy. Compd., 485, 573–576 (2009).
10) M. H. Lin, Ceram. Int., 31, 1109–1115 (2005).
11) J. Robertson, Mater. Sci. Eng., R37, 129–281 (2002).
12) J. Fontaine, T. L. Mogne, J. L. Loubet, and M. Belin, Thin Solid Films, 482, 99–108 (2005).
13) G. K. Williamson, and W. H. Hall, ActaMetallurgica, 1, 22–31 (1953).
14) K. Hokamoto, R. A. Pruemmer, R. Knitter, and K. Taira, J. Mater. Sci., 43, 684–688 (2008).
15) C. Yu, and J. Park, J. Solid State Chem., 183, 2268–2273 (2010).
16) Y. Zeng, T. Zhang, H. Yang, L. Qiao, Q. Qi, F. Cao, Y. Zhang, and R. Wang, Appl. Surf. Sci., 255, 4045–4049 (2009).



(a) Thin layer on the particle. (b) Enlarged image of thin layer.

Figure 8 TEM images of core shell structure particle.

流動パラフィン中におけるタングステン細線起爆による炭化タングステンの合成

田中茂*†，川路直樹*，和田直之*，外本和幸*

流動パラフィン中におけるタングステンの細線起爆によって，炭化タングステンのナノ粉末の合成に成功した。X線回折の結果，回収された粉末は大きく歪んだ立方晶のWC_{1-x}であることが分かった。TEM観察では，双晶の粒子や銅が薄く被覆したコアシェル構造の粒子を確認した。

*熊本大学　〒860−8555　熊本県熊本市中央区黒髪2丁目39番1号
Phone : 096−342−3902
†Corresponding author : tanaka@tech.eng.kumamoto-u.ac.jp