Mono-tungsten carbide (WC) and tungsten (W) have been successfully synthesized and classified by controlling organic–inorganic hybrid precursors. Tungstic acid (H₂WO₄) was dissolved into ammonium water and then citric acid (C₆H₈O₇) as a carbon source was dissolved into the H₂WO₄ solution. The precursors, which were obtained by drying the chemical complex solutions, were heated at 1473 K for 1 h with Ar gas flow by a conventional electric furnace. Classification of WC and W was achieved by controlling the precursor processing conditions. In terms of making WC only, two important processing factors were revealed. One, the C/W molar ratio of an organic–inorganic hybrid precursor should be more than 4.0, and two, the obtained chemical complex should be re-dissolved and aged for more than 24 h. Tungstic ions in the re-dissolved chemical complex solution may be changed into polyanions. The sizes of the obtained WC particles and W metal were approximately 100 nm and 2 μm, respectively.

©2013 The Ceramic Society of Japan. All rights reserved.

Key-words : Tungstic acid, Citric acid, pH, Polyanion

1. Introduction

Tungsten carbide (WC) is a promising candidate for various applications owing to its unusual properties, including a high melting point, superior hardness, low friction coefficient, high oxidation resistance, and superior electrical conductivity.¹ There are several methods of preparing tungsten carbide materials, including the direct carburization of tungsten metallic powder, solid-state metathesis, reduction carburization, mechanical milling, and polymeric precursor techniques using metal alkoxides.²,³ Generally, tungsten carbide production is a two-step process. First, the tungsten oxide is reduced to high-purity tungsten metal in a hydrogen atmosphere, and then, the tungsten metal is mixed with the required amount of carbon and reacts at a temperature of 1400–1600°C to produce tungsten carbide in a hydrogen atmosphere.⁴,⁵ The most important tungsten carbides are WC and W₂C. W₂C is thermodynamically unstable at low temperatures, while WC is stable, as confirmed by its electrochemical stability in acidic solutions.⁶ WC has been shown to have platinum (Pt)-like behavior for the chemisorptions of hydrogen and oxygen, and its applicability as an alternative electro-catalyst of Pt has been demonstrated.⁷ Previous studies have shown that this combination of an early transition metal with carbon yielded materials with attractive catalytic activity, stability, selectivity, and resistance to poisoning.⁸ WC has been considerably studied in hydrogenation, dehydrogenation, isomerization, and fuel cells because of its Pt-like catalytic activities, excellent stability, and CO poisoning tolerance.⁹,¹⁰ It has been reported in the synthesis of W₂C microspheres with high surface areas and chemisorptions capacity for use as a catalyst in direct methanol fuel cells (DMFCs).¹¹ Both WC and W₂C have shown their usefulness as catalysts in the DMFC catalyst research field.

Recently, highly pure nano-sized WC particles have been successfully prepared from organic–inorganic hybrid precursors by using a chemical complex solution.¹²,¹³ These methods have several advantages for processing nano-crystalline WC materials. Nano-crystalline WC can be available at relatively low temperatures (1273–1423 K) without requiring any hydrogen gas. In the present study, we report that synthesizing and classifying WC and W metals can be done by using the organic–inorganic precursor method.

2. Experimental

2.0 g of tungstic acid (H₂WO₄, MW = 249.85, Wako Chemical, Japan) powder was dissolved into 100 ml of ion-exchanged water with a 10-ml ammonium solution (28%, Wako Chemical, Japan). The H₂WO₄ solution was filtered to remove residual white dross. Citric acid (C₆H₈O₇, MW = 192.14, Wako Chemical, Japan) was then added to the H₂WO₄ solution as a carbon source. The molar ratio of carbon/tungsten (C/W) of the solutions was set to range from 1.0 to 6.0. The mixed solutions were placed in an oven and dried at 423 K in an air atmosphere. The obtained solid state matters, which were derived from the chemical complex solutions, were collected and called ‘first precursor’. These first precursors were dissolved into 100 ml of ion-exchanged water. The solution of the first precursors was stirred at room temperature for between 0 and 100 h. After aging, the solutions were again dried in an oven at 423 K in an air atmosphere. The organic–inorganic hybrid precursors for WC were then obtained.

The organic–inorganic hybrid precursor powders set on a carbon boat were heat-treated with an argon gas flow (100
Relationships between the organic–inorganic hybrid precursors and WC yield estimated from the XRD results are summarized in Fig. 2 as functions of the C/W molar ratio and the precursor aging time. Regardless of aging time, the final products derived from the precursors in the C/W molar ratio under 4.0 were pure tungsten metal. In a C/W molar ratio over 4.0, the final products were pure WC. Total carbon analysis of the obtained W metal was conducted by a combustion-infrared absorptiometrical method in reference to JIS-G1211. The measured total carbon was 0.46 mass %. Essentially, two main findings were revealed: 1) the organic–inorganic hybrid precursor for pure WC should be composed of a C/W molar ratio over 4.0, and 2) the first precursor should be aged for over 24 h. We speculate that the tungstic acid ions (WO$_4^{2-}$) in the precursor solutions were changed into polyanions during the aging treatment. The polyanions of the tungstic acid ions were expressed as [W$_4$O$_{16}$]$^{8-}$, [W$_6$O$_{19}$]$^{2-}$, [W$_{12}$O$_{40}$H$_2$]$^{10-}$, [HW$_{12}$O$_{40}$]$^{6-}$, [W$_{10}$O$_{32}$]$^{4-}$, and [W$_9$O$_{40}$]$^{2-}$.$^{15}$ We had expected that the appropriate conditions for forming complex molecules of the above shown tungstic polyanions and citric acids would be made possible by the aging treatment. First, the pH values of the first precursor solutions were very high due to the first addition of the ammonium solution for H$_2$WO$_4$ dissolving. Excessive ammonium ions may have disappeared as a gas from the solutions during the drying process of the first precursors. Next, the first precursors were re-dissolved into ion-exchanged water and given an aging treatment. Finally, it was found that the pH value of the precursor solution at which WC would be available was approximately 4.0. It is important when obtaining WC that the organic–inorganic hybrid precursor be given an aging time of over 24 h and kept at a C/W molar ratio over 4.0. However, the precursors exhibited no difference within the XRD patterns analysis, as shown in Fig. 1(d). Investigating the precursors in more detail will be our future work.

SEM micrographs of the synthesized powder materials are shown in Fig. 3. The crystalline size of the obtained WC was estimated to be approximately 100 nm within SEM observations, while that of the obtained W metal was estimated to be several micro meters. It may be possible to obtain smaller WC and W metal particles at processing temperatures lower than 1473 K. Both WC and W metal were observed to be aggregated, as shown in Fig. 3. There is no relationship between WC and W metal in terms of crystalline size. The above results demonstrate that WC and W metals can be synthesized and classified by controlling the organic–inorganic precursors.

![Fig. 1. X-ray diffraction patterns of obtained powder materials derived after aging precursors for 24 h in C/W molar ratios over 4.0 (a), just 4.0 (b), under 4.0 (c), and organic–inorganic hybrid precursor (d), respectively.](image-url)

![Fig. 2. Relationship between product phases and processing conditions (W/C molar ratio and aging time).](image-url)
4. Conclusions

We identified two important processing conditions necessary to obtain pure WC via the organic–inorganic precursors method. First, the organic–inorganic hybrid precursor should have a C/W molar ratio of over 4.0. Second, the dried first precursor should be re-dissolved into water and aged for over 24h. We were ultimately able to identify the appropriate processing conditions for synthesizing and classifying WC and W metals using the organic–inorganic hybrid precursor method.

Acknowledgement This research was partly supported by Hitachi Metals · Materials Science Foundation.

References

1) S. Shanmugan, D. S. Jacob and A. Gedanken, *J. Phys. Chem. B*, 109, 19056–19059 (2005).
2) S. V. Pol, V. G. Pol and A. Gedanken, *Adv. Mater. (Deerfield Beach Fla.)*, 18, 2023–2027 (2006).
3) S. V. Pol, V. G. Pol and A. Gedanken, *Eur. J. Inorg. Chem.*, 6, 709–715 (2009).
4) J. M. Girandon, P. Devassine, J. F. Lamonier, L. Delannoy, L. Leclereq and G. Leclereq, *J. Solid State Chem.*, 154, 412–416 (2000).
5) P. N. Ross, Jr. and P. Stonehart, *J. Catal.*, 39, 298–301 (1975).
6) M. G. Zellner and J. G. Chen, *Catal. Today*, 99, 299–307 (2005).
7) R. B. Levy and M. Boudart, *Science*, 181, 547–549 (1973).
8) H. Binder, A. Kohling, W. Kuhn and G. Sandstede, *Angew. Chem., Int. Ed. Engl.*, 8, 757–758 (1969).
9) H. H. Hwy and J. G. Chen, *Chem. Rev.*, 105, 185–212 (2005).
10) N. Ji, T. Zhang, M. Y. Zheng, A. Q. Wang, X. D. Wang and J. G. Chen, *Angew. Chem., Int. Ed.*, 47, 8510–8513 (2008).
11) C. Guordano, C. Erpen, W. T. Yao and M. Antonietti, *Nano Lett.*, 8, 4659–4663 (2008).
12) R. Ganesan and J. S. Lee, *Angew. Chem., Int. Ed.*, 44, 6557–6560 (2005).
13) Y. Yamashita, T. Harada, T. Makino, K. Fujiyoshi, S. Ueno and M. Koga, *J. Jpn. Soc. Powder Powder Metall.*, 57, 348–351 (2010).
14) D. Chen, H. Wen, H. Zhai, H. Wang, X. Li, R. Zhang, J. Sun and L. Gao, *J. Am. Ceram. Soc.*, 93, 3997–4000 (2010).
15) M. T. Pope and Y. Jeannin, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin Heiderberg New York Tokyo (1983) pp. 48–57.