

Preparation of $\text{Mo}_2\text{C}@a\text{-C}$ core-shell powders via carburization of Mo particles by 1-chlorobutane and hexachlorobenzene

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Received 19 July 2006; accepted 27 November 2006

Available online 19 December 2006

Abstract

$\text{Mo}_2\text{C}@a\text{-C}$ core-shell powders were prepared by reacting Mo powders with gaseous 1-chlorobutane or hexachlorobenzene at 1173 K. The chlorinated reactants acted as the source of carbon for the carburization of Mo and the source of chlorine, which assists the etching of Mo to reduced particle sizes.

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Keywords: Nanocomposites; Powder technology; Molybdenum carbide; Core-shell structure

1. Introduction

Molybdenum carbides are conventionally synthesized by a variety of methods, including, arc melting of Mo or its oxide with graphite, temperature-programmed reaction between molybdenum oxide and alkanes, and annealing mechanically activated mixture of amorphous carbon with molybdenum [1–6]. Recent reports have shown that it is possible to prepare Mo_2C through reduction–carburization. For example, high temperature reduction of MoCl_5 by a mixture of 20% of CH_4 in H_2 produced Mo_2C [7]. Reduction of MoO_3 powders by carbon black at high temperatures generated Mo_2C also [8]. Similar reaction methodology was employed to prepare activated carbon supported bimetallic carbide of molybdenum and tungsten [9]. Previously, we reported a method to synthesize titanium carbide via carburization of titanium powders by 1-chlorobutane [10]. In another study, we discovered that hexachloroethane could be used to carburize titanium and molybdenum surfaces [11]. In this report, we wish to discuss the result of carburization reaction of molybdenum powders by 1-

chlorobutane and hexachlorobenzene. Particularly, we found that $\text{Mo}_2\text{C}@a\text{-C}$ particles, with a structure of an Mo_2C core encapsulated in an amorphous carbon shell, can be produced under controlled reaction conditions.

2. Experimental procedure

In a typical reaction, Mo powders (1–3 μm , Riedel–deHaën) in a quartz boat were placed in a 30-mm quartz tube and heated by a horizontal tube furnace at 1173 K. At 1 atm, 1-chlorobutane (Janssen) at 298 K was bubbled into the reactor under a flow of Ar (20 sccm) for 8 h to produce a black powder. In another typical reaction, hexachlorobenzene (Aldrich) at 393 K under vacuum was vaporized and reacted with Mo powders at 1073 K for 24 h to generate a black powder. In all reactions, yellow and brown byproduct solids deposited at the outlet of the reactor wall. The solids turned green and blue when exposed to air. The black products were characterized by scanning electron microscopy (SEM, JEOL JSM-6330F at 15 kV), X-ray diffraction (XRD, Bruker D8 Advance, Cu $\text{K}\alpha$ radiation, 40 kV, and 40 mA), Raman spectroscopy (Jabin Yvon HR800 equipped with an Ar^+ laser at 514.5 nm), and X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI-1600, $\text{MgK}\alpha$ radiation at 1253.6 eV). Combustion elemental analyses

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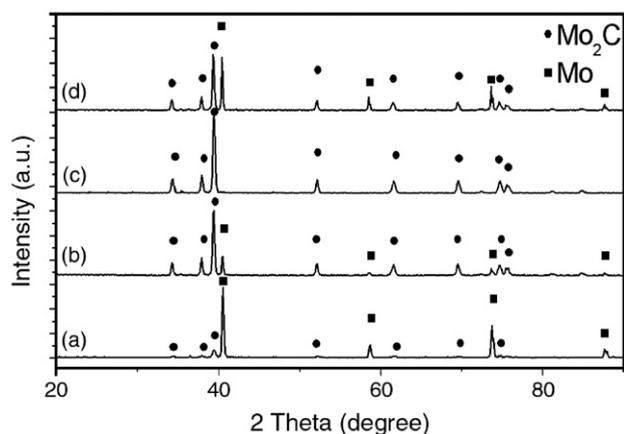


Fig. 1. XRD patterns of powders prepared from Mo and 1-chlorobutane at (a) 873 K, (b) 1073 K and (c) 1173 K under a flow of 20 sccm Ar for 8 h. (d) XRD pattern of a powders prepared from Mo and hexachlorobenzene at 1073 K under vacuum for 24 h.

were performed on a Heraeus CHN–O Rapid instrument to determine the carbon contents.

3. Results and discussion

XRD patterns of the solids produced by carburization of Mo powders by 1-chlorobutane and hexachlorobenzene at 873–1173 K for 8 h are shown in Fig. 1. Fig. 1(a) suggests that at 873 K, only a small

portion of the purchased Mo metal powders was carburized by 1-chlorobutane to form hexagonal Mo_2C [12,13]. At a temperature of 1073 K, the enhanced signals of Mo_2C , as shown in Fig. 1(b), suggest that the reaction proceeded at an increased rate. Fig. 1(c) shows the XRD pattern of the powder prepared at 1173 K. This suggests that the Mo powders were completely carburized at this temperature. Fig. 1(d) shows the XRD pattern of the sample obtained from the reaction between hexachlorobenzene and Mo at 1073 K. The result also indicates that some Mo was converted into hexagonal Mo_2C [12,13]. The reaction at 1173 K showed a complete carburization of Mo into Mo_2C in 8 h.

Fig. 2(a) shows an SEM image of aggregated particles prepared from 1-chlorobutane and Mo at 1073 K. EDS is used to study a particular particle marked by arrows 1 and 2. The area pointed by 1 is C-rich while the area indicated by 2 is composed mainly of Mo. In both areas, the signal from Cl is not observed. Fig. 2(b) is an enlarged view of the particle. Based on the image, the EDS data, and the XRD in Fig. 1(b), we propose that the particle has an inner Mo core with a diameter ca. 2 μm and an outer shell with a thickness ca. 0.5 μm . The shell is composed of Mo_2C and amorphous carbon (see below for amorphous carbon characterization). Fig. 2(c) shows an SEM image of the powders prepared from a reaction between hexachlorobenzene and Mo at 1073 K under vacuum. While the original profile of Mo particles is preserved, many holes appear on the surface. We speculate that chlorine atoms etched the Mo surface to form the structure. The process also created particles with reduced sizes. Fig. 2(d) reveals that these particles, with size 50–200 nm, aggregate together on the surface of Mo. The EDS indicates that the material is still Mo-rich. This is consistent with the XRD data in Fig. 1(d), showing the patterns of Mo_2C and Mo.

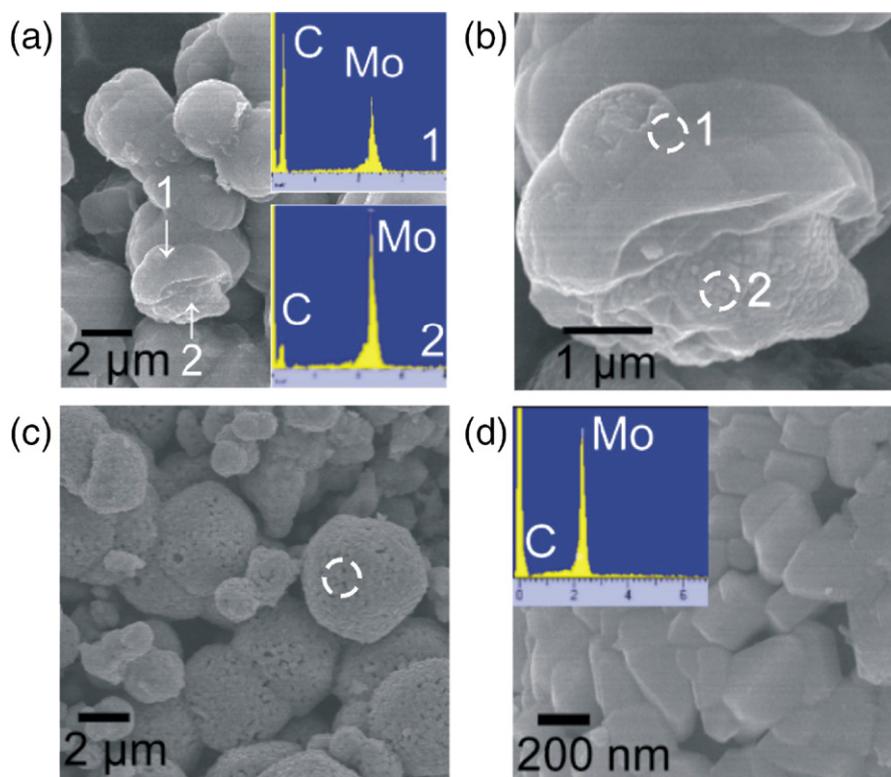


Fig. 2. (a) SEM image of a powder prepared from Mo and 1-chlorobutane at 1073 K under a flow of 20 sccm Ar for 8 h; inset: EDS from the spots indicated by arrows 1 and 2. (b) Enlarged SEM image of the particle shown in (a). (c) and (d) are SEM and EDS (inset) images of a powder prepared from Mo and hexachlorobenzene at 1073 K under vacuum for 24 h.

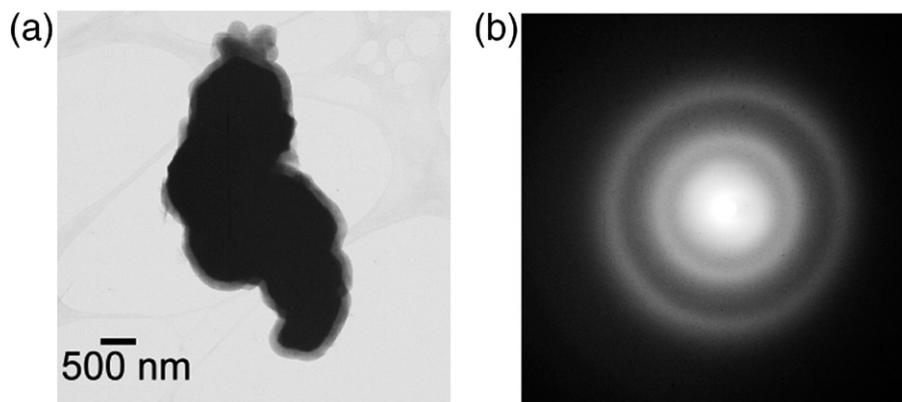


Fig. 3. (a) TEM image of a particle aggregate prepared from Mo and 1-chlorobutane at 1173 K under a flow of 20 sccm Ar for 8 h. (b) ED image of the bottom part of the aggregate shown in (a).

Fig. 3(a) shows a TEM image of aggregated particles prepared from 1-chlorobutane and Mo at 1173 K. The image suggests that the aggregate is covered by a shell with a thickness of ca. 200 nm. An electron diffraction (ED) pattern in Fig. 3(b) displays two weak diffused rings. They are indexed to (101) and (110) reflections of small graphite crystals [14]. Due to the sample thickness, the ED pattern of Mo_2C is not observed. Based on the images and XRD result in Fig. 1(c), we propose that the sample has an Mo_2C core covered by a less-ordered carbon shell. Even though some small graphite exists in the sample shell, the overall carbon orderness is low. The nearly amorphous nature of the carbon shell is further confirmed by the Raman study below.

Fig. 4 shows Raman spectra of the Mo powders carburized by 1-chlorobutane and hexachlorobenzene at different temperatures. The G-band (1589 cm^{-1}) and D-band (1353 cm^{-1}) vibrations suggest the formation of a carbon material. The peak intensity ratio, I_D/I_G , strongly suggests that the observed carbon material in each sample is non-crystalline [15]. The I_D/I_G ratios increase as the reaction temperature was raised from 873 K to 1173 K, as shown in Fig. 4(a)–(c). This suggests that orderness of the carbon atoms decreased slightly at raised reaction temperatures. Fig. 4(d) reveals that the sample, which was prepared by reacting hexachlorobenzene with Mo, also contains

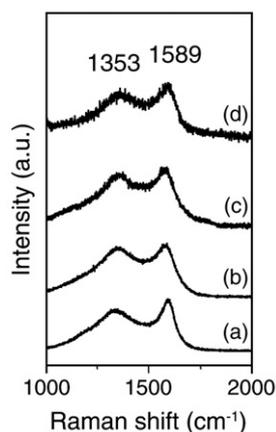


Fig. 4. Raman spectra of powders prepared from Mo and 1-chlorobutane at (a) 873 K, (b) 1073 K and (c) 1173 K under a flow of 20 sccm Ar for 8 h. (d) Raman spectrum of a powder prepared from Mo and hexachlorobenzene at 1073 K under vacuum for 24 h.

amorphous carbon. Fig. 5 shows the XPS survey data of a powder prepared from Mo and 1-chlorobutane at 1173 K under a flow of 20 sccm Ar for 8 h. In Fig. 5(a), the as-prepared sample shows the presence of Mo and C atoms. No Cl atoms can be detected on the surface. After the sample was sputtered by Ar^+ ion for 30 s, the survey shown in Fig. 5(b) indicates that except for the intensity of C diminishing slightly, the elemental composition is essentially the same. The carbon content of the sample prepared from Mo and 1-chlorobutane at 1173 K was further investigated by combustion elemental analysis. The result showed that the sample contained 11.68 wt.% of C. The theoretical carbon value in Mo_2C is only 5.89 wt.%. This suggests that the sample is carbon-rich. Based on this information and the other data shown in Figs. 1–5, we conclude that the material produced at 1173 K in this study is $\text{Mo}_2\text{C}@a\text{-C}$, a completely carburized Mo_2C core wrapped in an amorphous C shell.

A mechanistic model is proposed in Fig. 6 to show how an Mo particle is carburized by 1-chlorobutane to form Mo_2C . In the first step, 1-chlorobutane reacts with the Mo surface to deposit an a-C layer. The chlorine atoms combine with Mo atoms to generate volatile MoCl_x molecules, observed as solid deposits at the outlet of the reaction chamber [16]. In the next step, a reaction between a-C and Mo creates an interlayer of Mo_2C between the a-C shell and the Mo core. Finally,

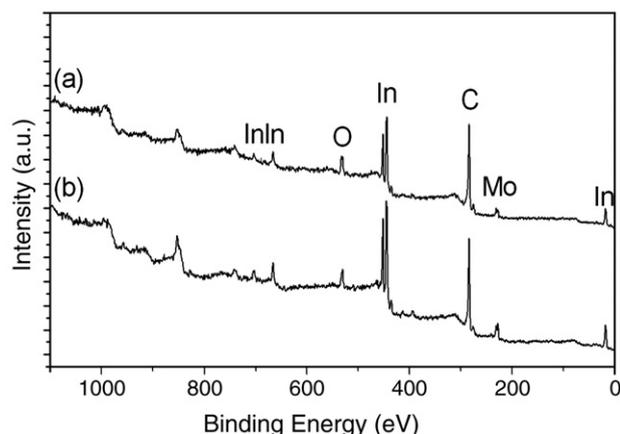


Fig. 5. XPS survey of powders prepared from Mo and 1-chlorobutane at 1173 K under a flow of 20 sccm Ar for 8 h. In metal was used as the sample support. (a) As-received and (b) after Ar^+ ion sputtering for 30 s.

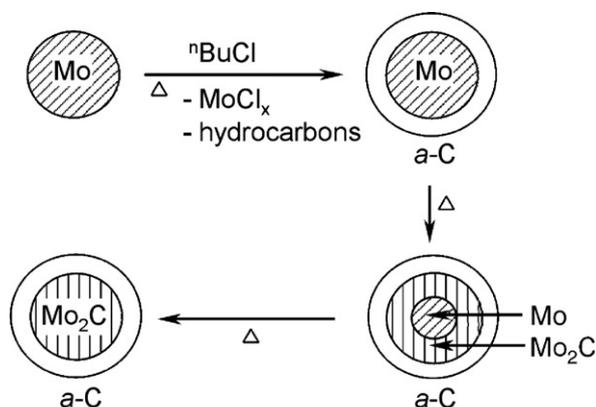


Fig. 6. Proposed reaction steps between $n\text{BuCl}$ and Mo to form an $\text{Mo}_2\text{C}@a\text{-C}$ particle.

further carbon diffusion through the Mo_2C layer causes the inner Mo core to carburize completely into the $\text{Mo}_2\text{C}@a\text{-C}$ structure. The reaction process between C_6Cl_6 and Mo powders probably proceeds similarly.

4. Conclusions

$\text{Mo}_2\text{C}@a\text{-C}$ powders have been synthesized from the reactions between Mo metal powders with 1-chlorobutane or with hexachlorobenzene at 1173 K. The chlorinated reactants not only act as the carbon source to carburize Mo powders but also covered the surface to form the core/shell structure. The other role of the chlorinated reactants is a source of chlorine atoms, which etched the metal into smaller particles.

Acknowledgements

We thank the National Science Council and the Ministry of Education of Taiwan, the Republic of China for their support.

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