Formation of Molybdenum Oxide Nano-whiskers during Heating Compressed Powder

S. M. M. Shafiei*, E. Salahi, S. A. Tayebi fard

Materials and Energy Research Center (MERC), I.R. Iran

(*) Corresponding author: Smm_shafiee@yahoo.com
(Received: 04 Jul. 2010 and Accepted: 30 Aug. 2010)

Abstract:
In this study the synthesis of molybdenum oxide nano-whiskers with circular cross-section is performed. In some areas, it was observed that also some whiskers have open tips exhibiting their hollow structures. These whiskers have side dimensions ranging 2-5 μm with an average diameter in the nanometer rang. The structure suggested the vapor-liquid-solid growth mechanism (VLS). Scanning electron microscopy (SEM) was used to characterize microstructure evolution of specimens treated by heating processes.
Keywords: *molybdenum oxide, Whiskers, synthesis, VLS mechanism*

1. INTRODUCTION

In recent years, much effort has been devoted to study of molybdenum oxide and related materials [1-3]. It has been shown that molybdenum oxide posses unique catalytic and electronic properties and have potential applications in chemical synthesis petroleum refining, recording media and sensors [4-6]. MoO_3 is the ultimate product of molybdenum oxidation compounds. It forms white orthorhombic crystal that is photosensitive, i.e., turn blue in light. The compound is weakly paramagnetic and n-type semiconductor. It is produced by roasting molybdenum disulfide in air at 600^{o}C and may be purified by sublimation. It can also be prepared by reacting ammonium molybdate at 550^{o}C with oxygen or by precipitation from an aqueous ammonium molybdate solution treated with concentrated nitric acid [7]. A variety of uses facilitates the development of novel synthesis methods for the generation of molybdenum oxides and related materials with desirable structure, chemical activity, and physical properties. For catalytic applications several techniques have been developed to synthesize nanodispersed molybdenum oxides directly on alumina and silica support surfaces [1]. MoO_2 is a dark blue crystalline solid and consists of chains of distorted MoO_6 octahedral. Molybdenum dioxide is a metallic conductor and is weakly paramagnetic. A number of studies have been devoted to the growth of MoO_2 nano-particles and wires on various substrates. Zhou and co-workers [4] have reported formation of MoO_2 nanowire arrays formed by employing a high temperature heating process in a restricted vacuum chamber. Alignment, vertical orientation and high degree of order are some of the physical characteristic of the formed nano wires. In the present study, synthesis of molybdenum oxide with circular cross-section is performed.

2. EXPERIMENTAL PROCEDURE

Cu (MERCK Art No.102703) and Mo (MERCK Art No. 12254) powders were used as starting materials. Cu powder was compressed under 250 MPa pressure and then Molybdenum powder as thin layer compressed on it under 250 MPa pressure. As-compressed specimens were heated in 973°K for 4 hours and were characterized by means of the X-ray diffraction method using CuK_a radiation. Scanning electron microscopy (Cambridge1990-6360) was used to characterize the microstructure evolution of the specimen treated by heating processes.

3. RESULTS AND DISCUSSION

Figure 1 shows x-ray diffraction pattern of MoO_3 which has been formed on the copper substrate.

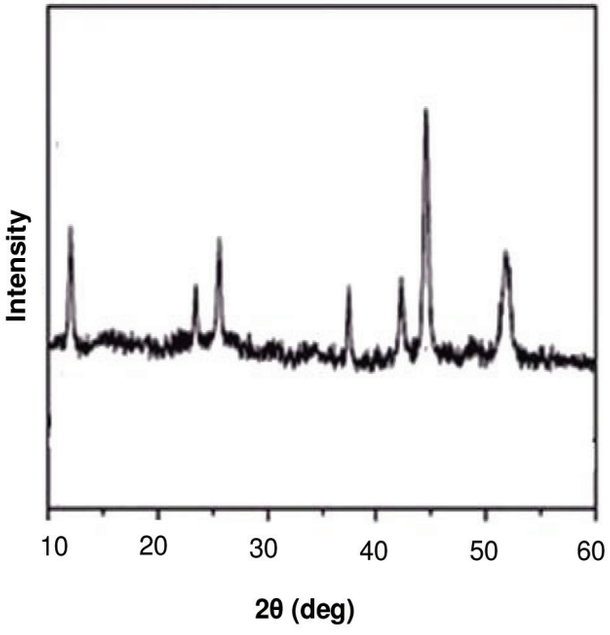

Figure 1: *The X-ray diffraction pattern of MoO_3 formed on the copper substrate*

Figure 2 represents SEM images of molybdenum with circular cross-section.

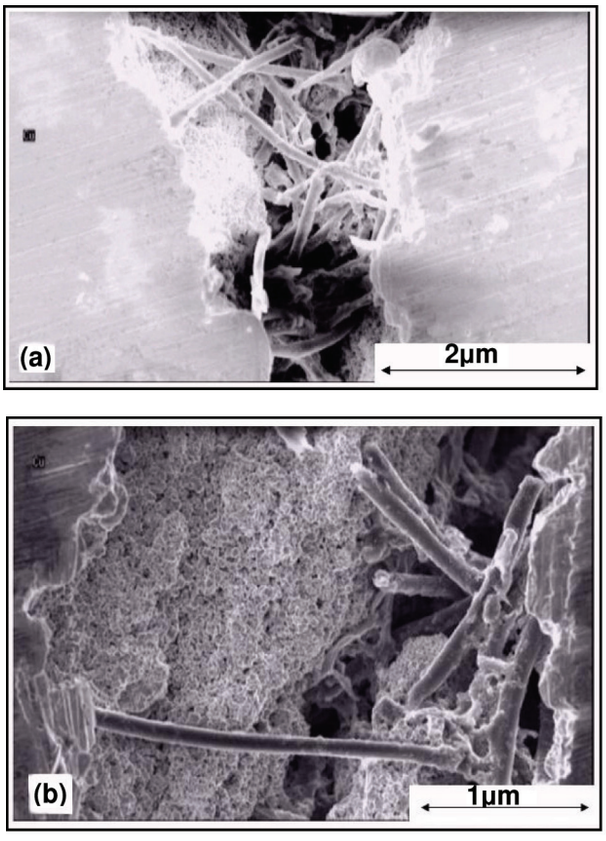

Figure 2: *(a) and (b) Representative SEM images of molybdenum oxide whiskers on the Cu surface*

The tips of the whisker have a dome capped shape suggesting the presence of liquid matter during the synthesis procedure (Figure 3).

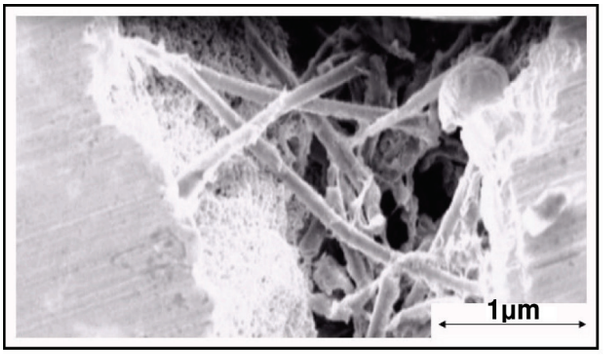

Figure 3: *SEM image of molybdenum oxide whiskers*

In some areas, it was also revealed that some whiskers have open tips exhibiting their hollow structure as shown in Figure 4.

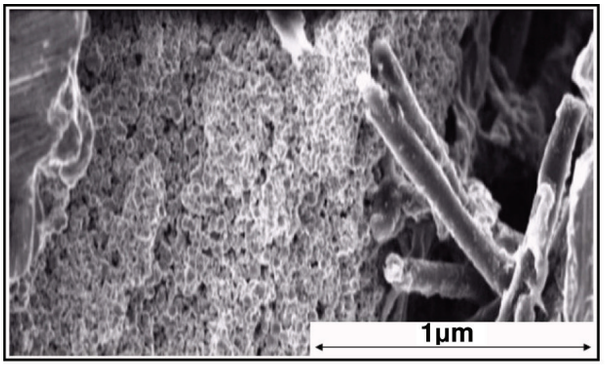

Figure 4: *SEM images of molybdenum oxide whisker exhibiting their hollow structure*

The wires have side dimensions ranging 2-5 µm with an average diameter that is in the nanometer rang. The structure suggested the vapor-liquid-solid growth mechanism (VLS). Under the influence of surface tension, a liquid particle formed on the tip of the growing wire acquires a semi-spherical shape that influences the formation of cylindrical wire body as shown in Figure 5.

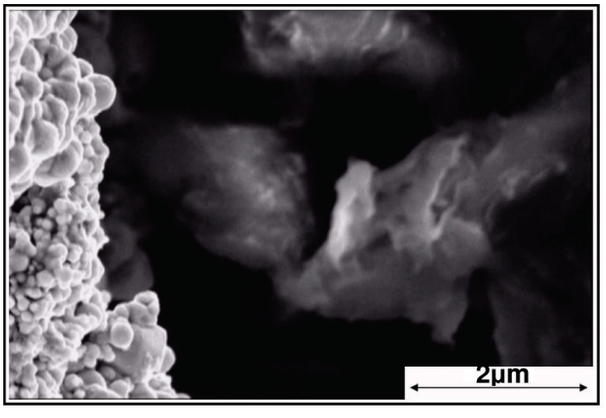

Figure 5: *SEM images of molybdenum oxide whisker shows the presence of liquid*

At first, a layer of MoO_2 is formed coating the Mo substrate, followed by a layer containing different molybdenum – oxides MoO_{3x-1} and finally by an outmost layer of MoO_3. Further whisker growth can proceed following vapor-liquid-solid or vapor-solid mechanism depending on the temperature and other process parameters. At high temperatures, liquid drops of composition are formed on the tips of the growing wires; they serve as intermediates that accept new material from the gas phase and convert it to crystals. The characteristic structures of the tips observed by SEM images partially confirmed this hypothesis. The vapor-liquid-solid mechanism and finite size of formed liquid droplets along with a low driving force of crystal growth (usually defined as a ratio of the chemical potential difference between two phases over temperature [8]) result in small cross-sectional sizes of the grown whiskers. The structures are well aligned and appeared to grow perpendicular to the surface of the surface. Their length is from 2 to 50 µm. The structures have very uniform shape. All of the present structures have an intriguing similarity in shape of their tips. The tips of the structures have a circular shape. It is observed that on the certain types of the grown structures the cross-sectional area at the middle of the objects tends to be largest and decreases at the bases and tips. Small plate is presented near the roots of the crystals suggesting development of dendrite structures.

4. CONCLUSIONS

The synthesis of molybdenum oxide solid whiskers with circular cross-section is performed on copper substrate. In some areas, it was also revealed that some whiskers have open tips exhibiting their hollow structure. The whisker has side dimensions ranging from 2 to 5 µm with an average diameter that is in the nanometer rang. The structure suggests the vapor-liquid-solid growth mechanism (VLS).

REFERENCE

1. N. A. Dhas, A. Gedanken, Chem. Mater. 9(1997): 3144.
2. M. Anpo, M. Kondo, Y. Kubokawa, C. Louis, M. Che, J. Chem. Soc., Faraday Trans. 1 (84) (1988): 771.
3. Y. Liu, Y. Qian, M. Zhang, Z. Chen, C.Wang, Mater. Res. Bull. 31 (1996): 1029.
4. J. Zhou, N. S. Xu, S.Z. Deng, J. Chen, J.C. She, Chem. Phys. Lett. 382 (2003): 443.
5. Z.W. Pan, Z. R. Dai, Z. L. Wang, Science 291 (2001): 1947.
6. Z. R. Dai, Z. W. oan, Z. L. Wang, Adv. Funct. Mater. 13 (2003): 9.
7. G. Brauer (Ed): Handbook of preparative Inorganic Chemistry, 2nd ed., vol. 2, Academic Press, New York, 1965, p.1412.
8. I. Sunagawa, Crystals. Growth, Morphology and Perfection, Cambridge University Press, Cambridge, 2005, p. 74.