Thermal plasma source for processing of MoO$_3$ crystals

A Lebid$^1$, A Veklich$^1$, V Boretskij$^1$, S Savenok$^2$ and O Andreev$^2$

$^1$ Taras Shevchenko National University of Kyiv, Faculty of Radio Physics, Electronics and Computer Systems, Kyiv, Ukraine
$^2$ Taras Shevchenko National University of Kyiv, Faculty of Geology, Kyiv, Ukraine

E-mail: tgctg@yandex.ru

Abstract. Simple original technique for fabrication of molybdenum trioxide MoO$_3$ crystals during electric arc discharge directly from metallic molybdenum was proposed. The vertically oriented free-burning arc was ignited between the end surfaces of metallic molybdenum non-cooled electrodes. Molybdenum oxide crystals were deposited on side surface of bottom electrode (anode). Observation of crystals formation zone was used for determination of main process stages. The resulting products were studied by X-rays diffraction and optical microscopy methods. Investigations indicate, that self-organizing vapor-deposition process of MoO$_3$ crystals formation has place. The resulting product is colorless sparkling prisms and platelets, which mainly consist of orthorhombic $\alpha$-MoO$_3$ phase. Optical microscopy indicates formation of closely packed feather-like pins structures by vapor-solid process.

1. Introduction

Molybdenum trioxide MoO$_3$ attracts scientific interests due to it’s unique physicochemical properties. There are useful applications of this material:

- as perspective material for lithium-ion batteries [1,2];
- as highly field emission cathode for display devices [3];
- as catalyst for hydrocarbons transformation reactions [4];
- as material for thin film gas sensors [5].

Fabrication of MoO$_3$ usually is performed by chemical or physical methods. The physical methods allow to obtain micro- and nano- structured materials, particularly crystals. These methods are mainly based on vapor-deposition processes. These processes are organized by evaporation of molybdenum or molybdenum oxide powders in special furnace [1,7], evaporation of molybdenum foil by infra-red heating [3], atmospheric plasma processes based on UHF discharge [2,6].

In the work [1] $\alpha$-MoO$_3$ obtained by vapor transportation method for application in lithium-ion rechargeable batteries was studied. Molybdenum trioxide powder was evaporated inside tube furnace in argon flow. Microstructured material was deposited on quartz substrate near the open side of furnace. It takes 1 hour to produce the final material as white $\alpha$-MoO$_3$ microrods at temperature 780-800°C. Lithium-ion battery cells, fabricated with using the microstructured $\alpha$-MoO$_3$ had higher...
stability and capacity in comparison with non-structured MoO₃ and other materials. These advantages are explained by tolerance of orthorhombic α-MoO₃ structure to intercalation/deintercalation of lithium ions during battery charging/discharging processes.

Atmospheric microplasma process was used in work [2] for preparation of monoclinic β-MoO₃ nanosheets. Molybdenum wire (Ø 0.1 mm) was sputtered by plasma of ultra high frequency (UHF) antenna discharge. Duration of nanomaterial deposition on Si-Pt substrate at atmosphere conditions was 45 s. Obtained material β-MoO₃ is very attractive due to its specific crystal structure, electrochemical properties and morphology for lithium battery and catalytic applications.

Other configuration of atmospheric microplasma process for molybdenum oxide was studied in work [6]. Molybdenum wire was closed inside quartz capillary with 60-70 μm nozzle. UHF discharge was initiated inside capillary by coil antenna. Reaction products transported by argon-oxygen mixture with various flow rates. Resulting nanoparticles are injected from nozzle on the silicon substrate. It was found that percentage of different oxides MoO₂ and MoO₃ in resulting particles was drastically affected by gas mixture flow rate. The changing of particle generation mechanism explains this phenomenon.

This paper deals with alternative technique, which allows formation of MoO₃ crystals directly from metallic molybdenum in electric arc plasma source at atmospheric pressure. Advantages of the technique are simplicity of equipment and conditions, self-organization of process and high reproducibility of resulting products.

2. Setup description

The vertically oriented free-burning arc was ignited in air between the end surfaces of metallic molybdenum non-cooled electrodes (figure 1, a). The diameter of the rod electrodes was 6 mm, the discharge gap was 8 mm and DC current was 3.5 A. Molybdenum oxide crystals were deposited on side surface of anode (figure 1, b). It must be noted, that zone of crystals formation has place at 3-5 mm below the end surface of electrode.

![Figure 1](image1.png)

**Figure 1.** Experimental scheme (a) and common view of anode with deposited MoO₃ crystals (b).

Video registration of crystal formation zone was used for determination of main process stages. Chemical composition and structure of obtained crystals were determined by X-rays diffraction method, performed by DRON-UM1 setup. Peculiarities of crystals formation were studied by optical microscopy method with using of MBI-1 microscope.
3. Formulation of crystals

The process of crystals formation during arc discharge can be separated on specific sequential stages. Immediately after arc ignition there wasn’t evaporation due to relatively low temperature of anode surface (figure 2, a).

After few seconds a white fume was observed around the electrode (figure 2, b). This stage was explained by oxidation of metallic molybdenum and volatilization of oxides at increasing electrode temperature. Really, oxidation of metallic molybdenum surface and volatilization of oxide layer were observed during heating in the furnace [1,7]. It was mentioned in work [7] that oxide layer completely evaporates from molybdenum surface at temperature above 1150°C. So, this assumption explains the absence of crystals near the end surface of electrode (figure 1) where surface temperature was obviously more higher.

The MoO$_3$ crystallites on electrode surface appeared at the next process phase (figure 2, c). Crystals start growing from white fume evaporations, which are transported by convectional air flow. Probably, initial crystallization starts on surface defects or on greyish-black particles, which can be Mo$_2$O$_3$. Friable layer around electrode (figure 1, b), which consists of variously oriented transparent prisms and platelets, was formed by vapor deposition.

Re-evaporation of deposited crystals is avoided by two reasons. The first one is low thermal conductivity between electrode and crystallites due to their irregular orientation. The crystallites are weakly connected to electrode surface but have numerous connection with others. The second reason is cooling of crystallites by convectional flows.

Therefore, in proposed plasma source self-organizing vapor-deposition process of MoO$_3$ crystals formation has place. The process consists of molybdenum surface oxidation, evaporation of oxide layers, vapour transportation by convectional air flow and crystal growth.

Usually formation of crystals is terminated after 2 min after arc ignition. It can be explained by overlapping of molybdenum surface by crystals, which complicates following evaporation and transportation of building material.
4. Chemical composition and structure

Chemical composition and structure of produced crystals were determined by X-rays diffraction method (XRD). Obtained crystals were detached from electrode surface and milled before the investigations. X-ray diffraction study indicates that resulting crystals consist of orthorhombic α-MoO$_3$ phase (figure 3). Positions of diffraction peaks are in good agreement with reference data [8]. High intensity of some diffraction peaks can be explained by orientation effects in structure of obtained crystalline material. Only slight admixture of monoclinic β-MoO$_3$ phase was detected.

Two forms of deposited crystals has place. The prismatic transparent crystallites with longitudinal dimension up to 3 mm and flat platelets with dimensions up to 3x3 mm are obtained.

Optical microscopy indicates formation of closely packed feather-like structures (figure 4). Every “feather” consists of closely packed parallel needles, which are unfinished structures of directional crystal growth. These needles are resembled to microrods observed in work [1], but in contrast, these microrods were oriented in a random way. Probably, attaching of building material on these pins has place during vapor deposition process and supports further translation of crystal structure.
Conclusions

Plasma source for processing of MoO$_3$ crystals directly from metallic molybdenum is proposed. XRD analysis indicates that resulting crystals mainly consist of orthorhombic $\alpha$-MoO$_3$ phase and only slight admixture of monoclinic $\beta$-MoO$_3$ phase was detected. The crystals are prismatic transparent prisms and flat platelets with dimensions up to 3 mm.

Formation of closely packed feather-like structures was observed. Every “feather” consists of parallel needles – unfinished structures of directional crystal growth.

So, self-organizing vapor-deposition process of MoO$_3$ crystals formation has place in proposed plasma source. Observation of crystal formation zone allows to conclude the further process mechanisms: molybdenum surface oxidation, evaporation of oxide layer, vapour transportation by convectional air flow and crystal growth.

Acknowledgement

The authors would like to thank to Professor Sergiy A. Vyzhva and Doctor Ida L. Babich for the help in organization of experiment and preparing of the paper.

References

[1] Li W, Cheng F, Tao Z, and Chen J 2006 Vapor-transportation preparation and reversible lithium intercalation/deintercalation of $\alpha$-MoO$_3$ microrods J. Phys. Chem. B 110 119-124
[2] Mariotti D, Lindstrom H, Chandra Bose A and Ostrikov K 2008 Monoclinic $\beta$-MoO$_3$ nanosheets produced by atmospheric microplasma: application to lithium-ion batteries Nanotechnology 19 495302
[3] Li Y B, Bando Y, Golberg D and Kurashima K 2002 Field emission from MoO$_3$ nanobelts Appl. Phys. Lett. 81 5048-50
[4] Queeney K T and Friend C M 2000 Site-Selective Surface Reactions: Hydrocarbon Oxidation Processes on Oxidized Mo(110) J. Phys. Chem. B 104 409-415
[5] Comini E, Faglia G, Sberveglieri G, Cantlini C, Passacantando M, Santucci S, Li Y, Wlodarski W and Qu W 2000 Carbon monoxide response of molybdenum oxide thin films deposited by different techniques Sensors and Actuators B 68 168-174
[6] Chandra Bose A, Shimizu Y, Mariotti D, Sasaki T, Terashima K and Koshizaki N 2006 Flow rate effect on the structure and morphology of molybdenum oxide nanoparticles deposited by atmospheric-pressure microplasma processing Nanotechnology 17 5976-82
[7] Vahldiek F W 1968 Growth and microstructure of molybdenum oxide Journal of the Less-Common Metals 16 351-359
[8] Powder diffraction files. Pdf-2 2013 The International Centre for Diffraction Data (Available from: http://www.icdd.com/products/pdf2.htm)