Electric arc plasma source: spectroscopy and MoO_3 crystal formation

A. Lebid, A. Veklich, V. Boretskij, S. Savenok, O. Andreev

Taras Shevchenko National University of Kyiv, Faculty of Radio Physics, Electronics and Computer Systems, Kyiv, Ukraine

This paper deals with alternative technique, which allows formation of MoO_3 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. The crystals are prismatic transparent prisms and flat platelets with dimensions up to 3 mm. The peculiarity of crystal was closely packed structures, which consists of parallel needles–unfinished structures of directional crystal growth.

1. Introduction

Fabrication of MoO_3 is performed usually 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. Such kind of processes are organized by evaporation of molybdenum or molybdenum oxide powders in special furnace [1,2], evaporation of molybdenum foil by infra-red heating [3], atmospheric plasma processes based on UHF discharge [4,5].

Molybdenum trioxide MoO_3 has some unique physicochemical properties. It can be used as perspective material for lithium-ion batteries [1,4]; as highly field emission cathode for display devices [2]; as catalyst for hydrocarbons transformation reactions [6] and as material for thin film gas sensors [7].

The aim of this work is investigations of peculiarities of crystal formation in the electric arc plasma source.

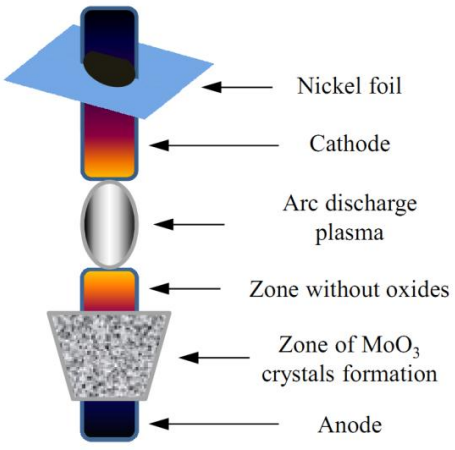
2. Plasma source and setup

The vertically oriented free-burning arc was ignited in air between the end surfaces of metallic molybdenum non-cooled electrodes (Fig. 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 appears on side surface of anode (Fig. 1, b) during arcing. It must be noted, that zone of crystals formation has place at 3-5 mm below the end surface of electrode.

The middle cross-section of electric arc discharge plasma was studied by optical emission spectroscopy technique [8]. The realized configuration of experimental setup (Fig. 2) with diffraction grating 600 g/mm permits simultaneous registration of spatial intensity distribution in spectral range 400-660 nm.

Video registration of crystal formation zone was used for determination of main process stages.

Peculiarities of crystal structure were studied by optical microscopy method with using of MBI-1 microscope.



a

b

Fig. 1. Experimental scheme of electric arc plasma source (a) and general view of anode with deposited MoO_3 crystals (b)

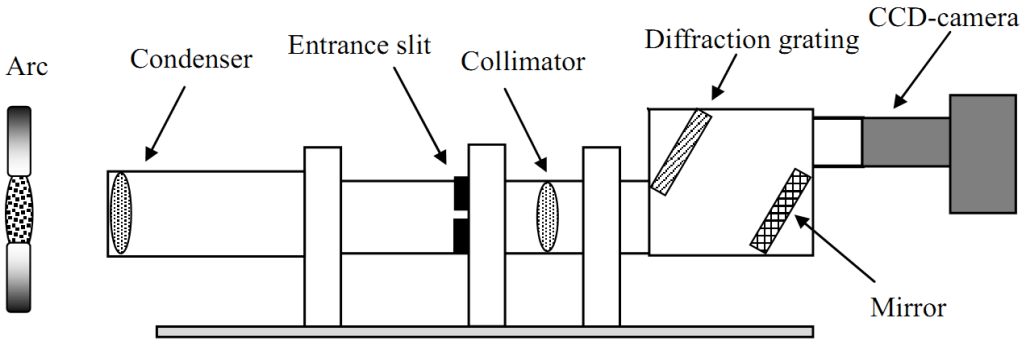


Fig. 2. Optical scheme of proposed experimental setup for emission spectroscopy

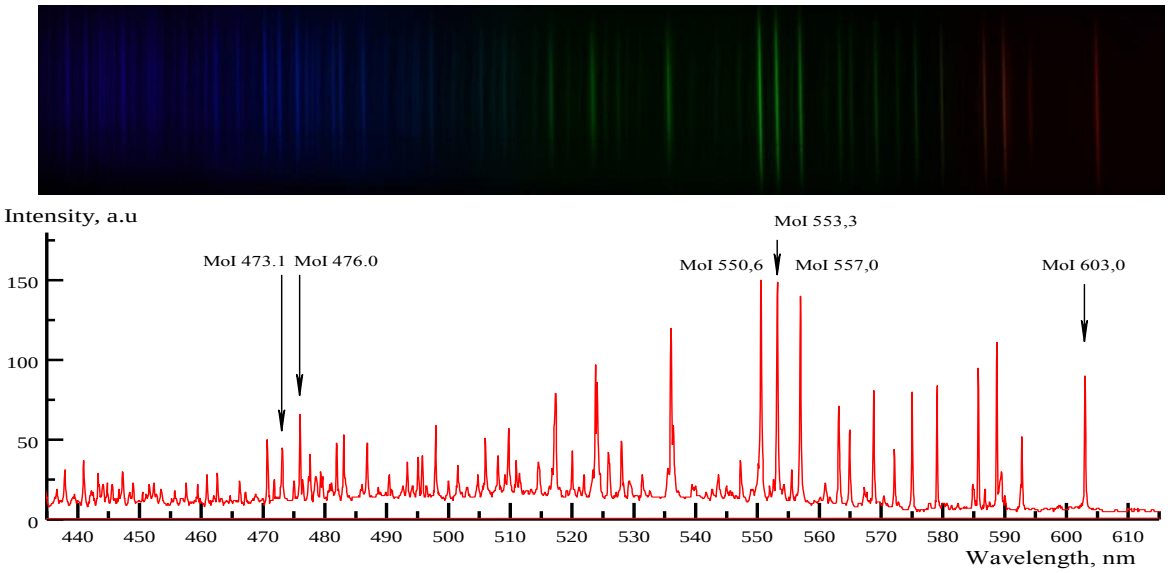


Fig.3. Registered spectrum and it's interpretation

Chemical composition and structure of obtained crystals and evaporation products were determined by X-rays diffraction method.

3. Crystal formation process

Optical emission spectroscopy, namely Boltzmann plot method was used for determination of plasma temperature. MoI spectral lines 473.1, 476.0, 550.6, 553.3, 557.0 and 603.0 nm (fig. 3) and preliminary selected spectroscopic data [9] were used. The temperature was estimated as 8000 K (fig. 4) at axial point in the middle cross-section of plasma.

4. Crystal formation process

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 (Fig. 5,a). After few seconds a white fume was observed around the electrode (Fig. 5, 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 [1,2].

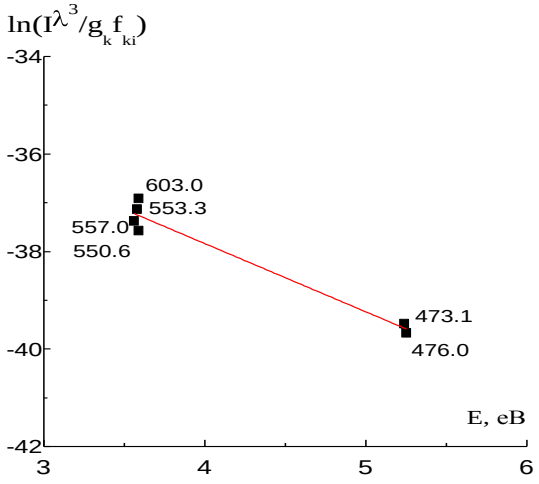
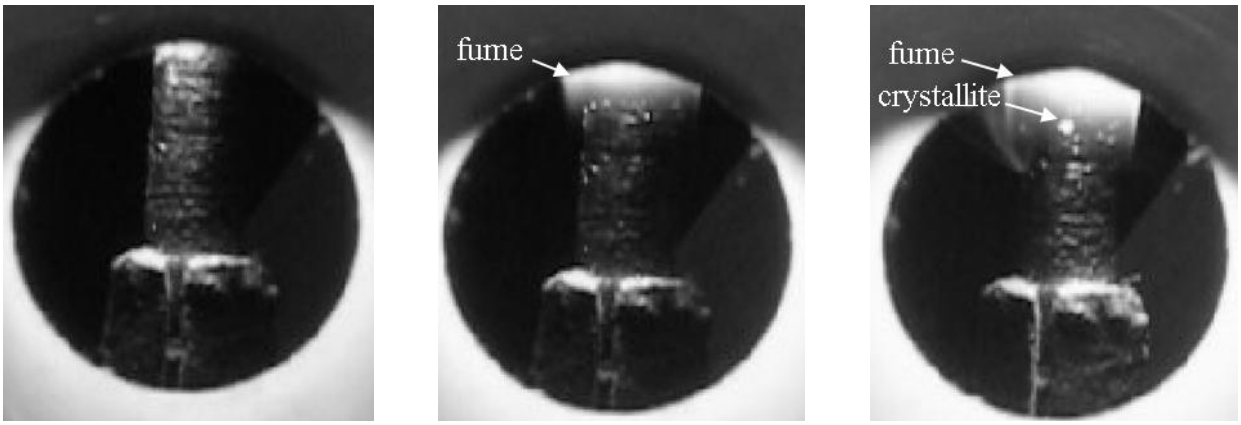


Fig.4. Boltzmann plot for emission from central point in middle cross-section of discharge gap



a b c

Fig. 5. View of anode at different process stages. Initial view - 7 s after arc ignition (a), appearance of white fume at 17 s (b), formation of MoO_3 crystallites at 25 s (c)

It was mentioned in work [2] that oxide layer completely evaporates from molybdenum surface at temperature above 1150^o C. So, this assumption explains the absence of crystals near the end surface of electrode (see Fig. 1,b) where surface temperature was obviously more higher.

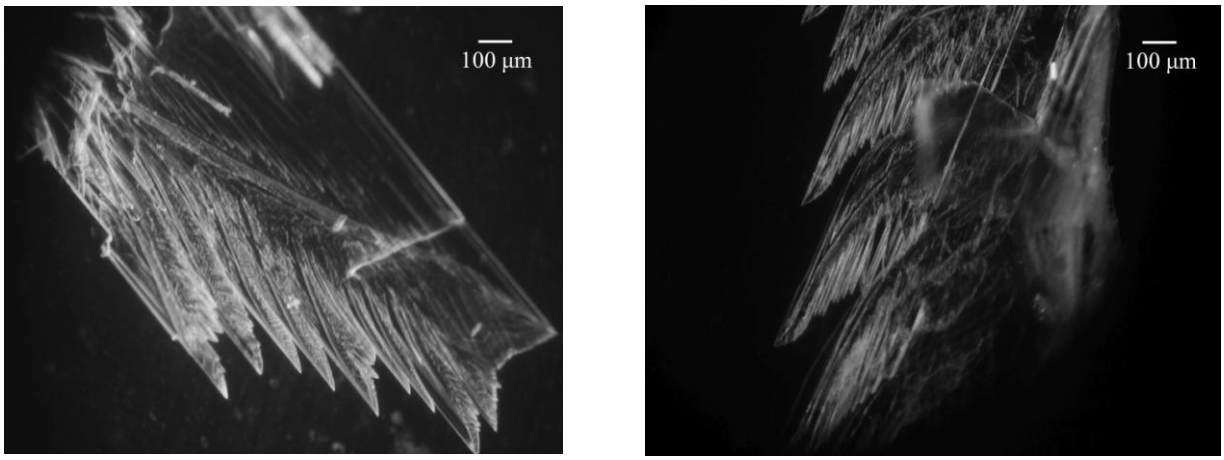
The MoO_3 crystallites on electrode surface appeared at the next process phase (Fig. 5,c). Crystals start growing from white fume evaporations, which are transported by convectional air flow. Probably, initial crystallization starts on surface defects or on greyish-black particles, which can be Mo_2O_3. Friable layer around electrode, which consists of irregular oriented transparent prisms and platelets (see Fig. 6), 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.

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.

Two forms of deposited crystals has place. The prismatic transparent crystallites with longitudinal dimension up to 3 mm and flat platelets (Fig. 6) with dimensions up to 3x3 mm are obtained.

Optical microscopy indicates formation of closely packed feather-like unfinished structures of directional crystal growth (see Fig. 6 a,b). They are consists of closely packed parallel needles. Probably, attaching of building material on these pins supports further translation of crystal structure.



a b

Figure 6. Optical microscopy of crystals growth structures.

Obtained crystals were detached from electrode surface and milled before the investigations. X-ray diffraction (XRD) study indicates that resulting crystals consist of orthorhombic α-MoO_3 phase (see Fig. 7). Positions of diffraction peaks are in good agreement with reference data [10]. High intensity of some diffractionpeaks can be explained by orientation effects in structure of obtained crystalline material. Only slight admixture of monoclinic β-MoO_3 phase was detected.

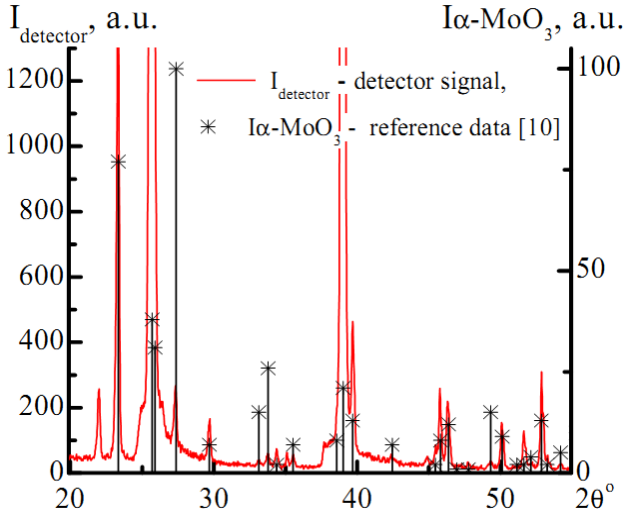


Fig. 7. XRD diagrams for MoO_3 crystals

Conclusins

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.

References

[1] W. Li, F. Cheng, Z. Tao, J. Chen. Vapor-transportation preparation and reversible lithium intercalation / deintercalation of α-MoO_3 microrods // *J. Phys. Chem. B* **110** (2006) 119-124.

[2] F.W. Vahldiek. Growth and microstructure of molybdenum oxide // *Journal of the Less-Common Metals* **16** (1968) 351-359.

[3] Y.B. Li, Y. Bando, D. Golberg and K. Kurashima. Field emission from MoO_3 nanobelts // *Appl. Phys. Lett.* **81** (2002) 5048-5050.

[4] D. Mariotti, H. Lindstrom, A. Chandra Bose, K Ostrikov. Monoclinic β-MoO_3 nanosheets produced by atmospheric microplasma: application to lithium-ion batteries // *Nanotechnology*, **19** (2008) 495302.

[5] A. Chandra Bose, Y. Shimizu, D. Mariotti, T. Sasaki, K. Terashima, N. Koshizaki. Flow rate effect on the structure and morphology of molybdenum oxide nanoparticles deposited by atmospheric-pressure microplasma processing // *Nanotechnology* **17** (2006) 5976-5982.

[6] K.T. Queeney, C.M. Friend. Site-Selective Surface Reactions: Hydrocarbon Oxidation Processes on Oxidized Mo (110) // *J. Phys. Chem. B*, 2000, v. 104, № 3, p. 409-415.

[7] E. Comini , G. Faglia, G. Sberveglieri, C. Cantlini, M. Passacantando , S. Santucci, Y. Li, W. Wlodarski, W. Qu. Carbon monoxide response of molybdenum oxide thin films deposited by different techniques // *Sensors and Actuators* **68** (2000) 168-174.

[8] A. Veklich, A. Lebid Technique of electric arc discharge plasma diagnostic: peculiarities of registration and treatment of spectra // *Bulletin of Taras Shevchenko National University of Kyiv. Radiophysics and electronics* **18** (2012) 6-9.

[9] A. Veklich. A. Lebid, T. Tmenova, V. Boretskij Spectroscopic investigations of electric arc plasma with additions of copper and molybdenum *XXXI International Conference on Phenomena in Ionized Gases* (2013) E-book of abstracts.

[10] Powder diffraction files. Pdf-2. *The International Centre for Diffraction Data* (2013) (www.icdd.com/products/pdf2.htm).