FORMATION OF MoO_3 CRYSTALS IN ELECTRIC ARC PLASMA SOURCE

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Formation of molybdenum trioxide crystals by electric arc discharge between molybdenum electrodes is considered. Molybdenum oxide crystals were deposited on side surface of anode. Observation of crystals formation zone was used for determination of main formations stages. Plasma temperature was estimated by optical emission spectroscopy method. The resulting products were studied by X-rays diffraction, time-of-flight laser mass-spectrometry and optical microscopy methods. It was found, that self-organizing vapor-deposition process of MoO_3 crystals formation has place. The resulting product is colorless sparkling prisms and platelets, which are mainly consist of orthorhombic α-MoO_3 phase. Optical microscopy indicates the formation of closely packed feather-like pin structures by vapor-solid process.

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INTRODUCTION

Molybdenum trioxide MoO_3 has some unique physicochemical properties. It can be used 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] and 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. Such kind of processes are organized by evaporation of molybdenum or molybdenum oxide powders in special furnace [1,6], evaporation of molybdenum foil by infra-red heating [3], atmospheric plasma processes based on UHF discharge [2, 7].

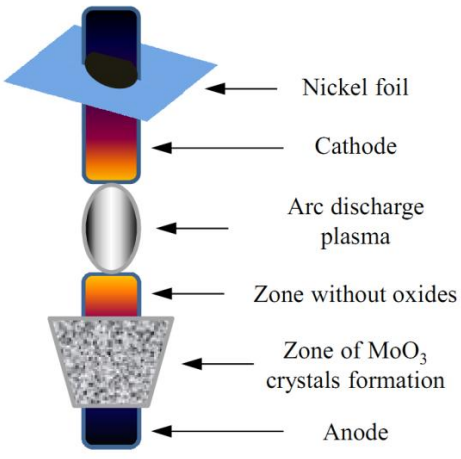
The aim of this work is determination of peculiarities of crystal formation in the electric arc plasma source.

1. EXPERIMENTAL TECHNIQUES

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 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 (a) and general view of anode with deposited MoO_3-crystals (b)

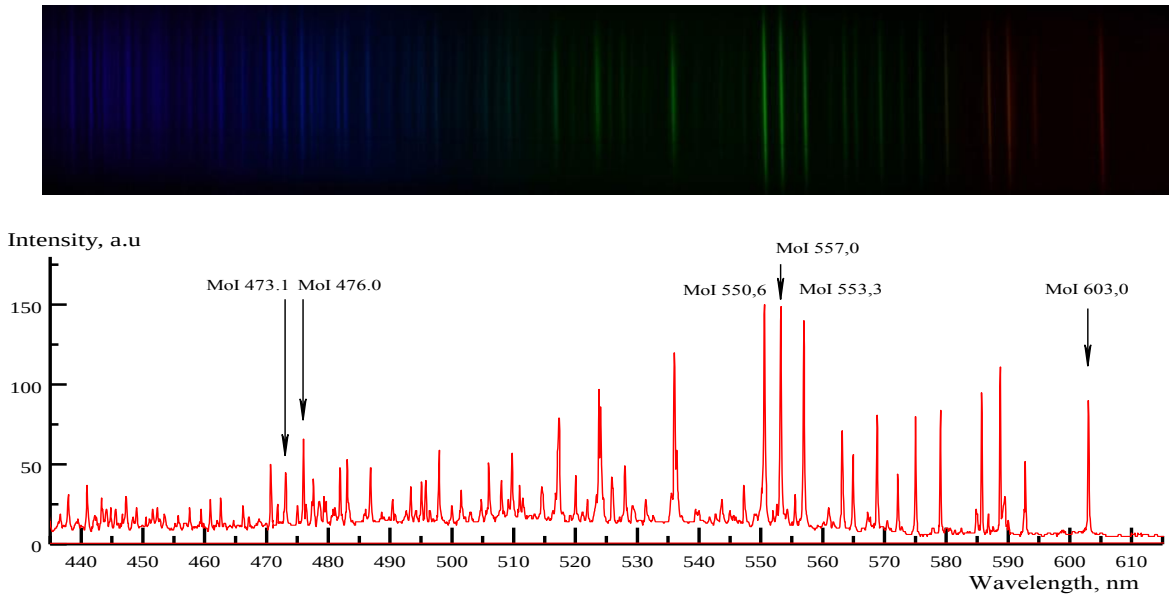


Fig. 2. Registered spectrum and it's interpretation

Chemical composition and structure of obtained crystals and evaporation products were determined by X-rays diffraction method and time-of-flight laser mass-spectrometry.

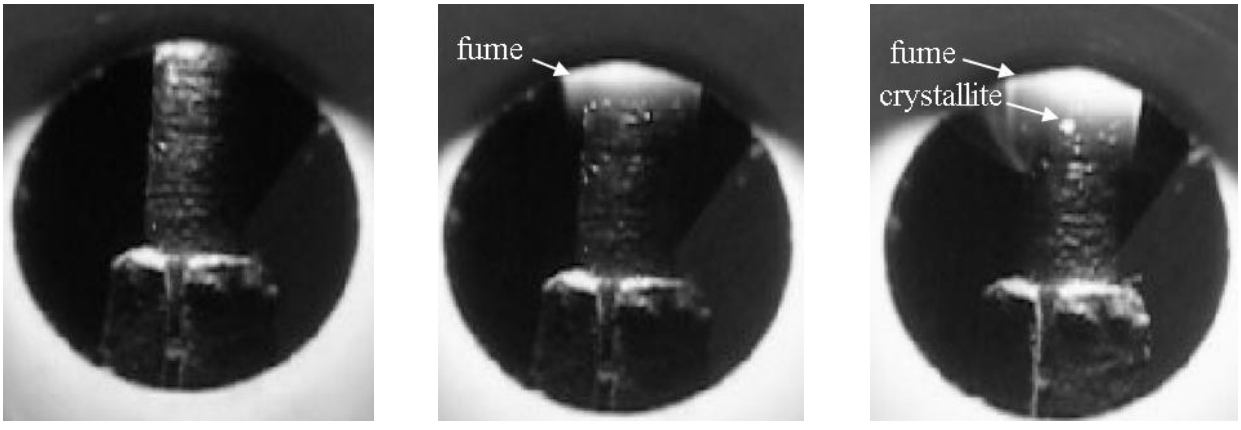
2. RESULTS AND DISCUSSIONS

2.1. PLASMA SPECTROSCOPY

Optical emission spectroscopy and 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. 2) and preliminary selected spectroscopic data [9] were used. The temperature in the middle cross-section of plasma was estimated as 8000 K.

2.2. CRYSTAL FORMATION

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. 3,a).



a *b* *c*

Fig. 3. 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)

After few seconds a white fume was observed around the electrode (Fig. 3, 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 furnance [1, 6]. It was mentioned in work [6] 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 (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. 3,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 (see Fig. 1,b), which consists of irregular 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.

2.3. CHEMICAL COMPOSITION AND STRUCTURE

Chemical composition and structure of produced crystals were determined by time-of-flight laser mass-spectrometry (Fig. 4) and X-rays diffraction method (Fig. 5, a,b). 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. 5, a). Positions of diffraction peaks are in good agreement with reference data [10]. High intensity of some diffraction peaks can be explained by orientation

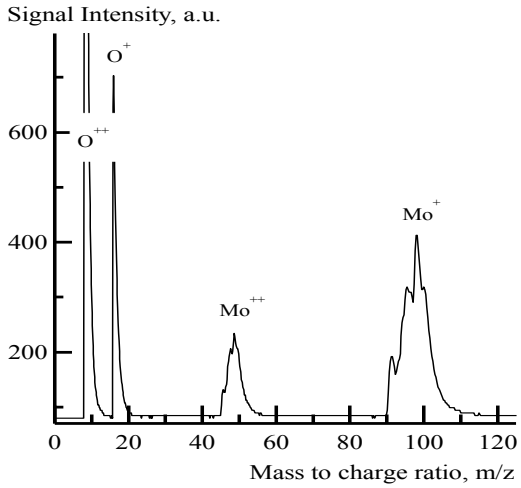


Fig. 4. Time of flight mass-spectrometry diagram for obtained crystals

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 (Fig. 6) with dimensions up to 3x3 mm are obtained.

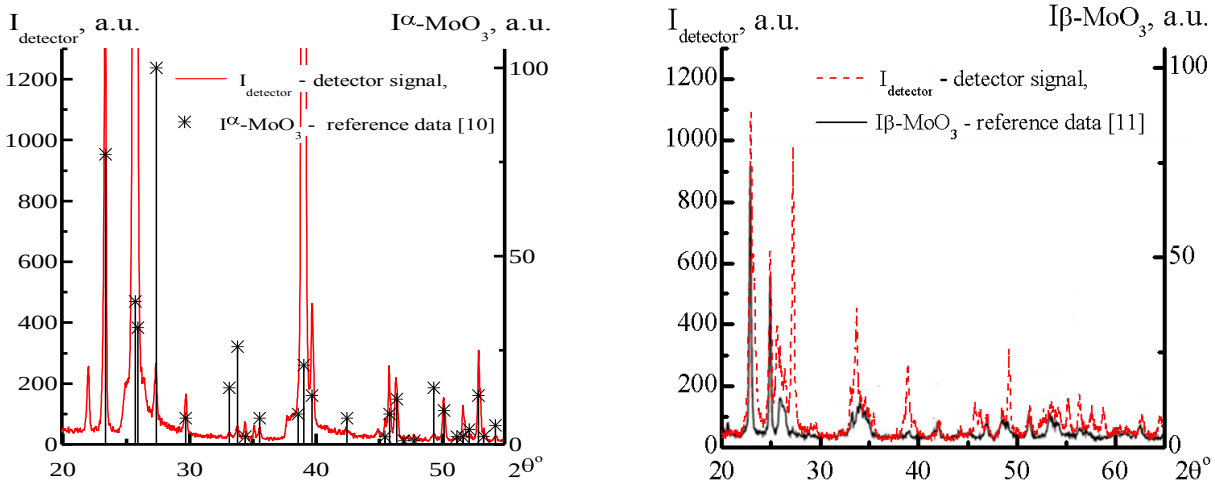


Fig. 5. XRD diagrams for MoO_3-crystals (a) and evaporation products deposited on nickel foil (b)

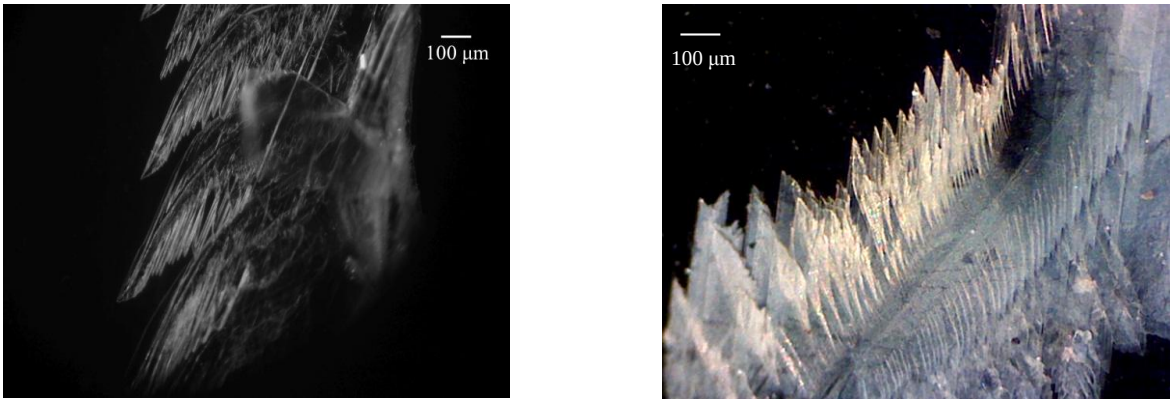


Fig. 6. Optical microscopy of crystals growth structures

Optical microscopy indicates formation of closely packed feather-like structures (see Fig. 6 a,b). Every "feather" consists of closely packed parallel needles, which are unfinished structures of directional crystal growth. Probably, attaching of building material on these pins has place during vapor deposition process and supports further translation of crystal structure.

Additionally evaporation products were collected on mounted above the cathode nickel foil (see Fig. 1,b). The deposited material also consists of MoO_3, but the content of β-MoO_3 in powder is significantly higher than in crystals. The ratio α-MoO_3 / β-MoO_3 can be estimated from XRD peak intensities (Fig. 5, b).

CONCLUSIONS

The temperature of plasma in the middle cross-section of electric arc discharge source was estimated as 8000 K.

The following stages of crystal formation were found: molybdenum surface oxidation, evaporation of oxide layer, vapour transportation by convectional air flow and crystal growth.

The crystals are prismatic transparent prisms and flat platelets with dimensions up to 3 mm. The peculiarity of crystal was closely packed feather-like structures. Every "feather" consists of parallel needles–unfinished structures of directional crystal growth.

XRD analysis indicates that resulting crystals mainly consist of orthorhombic α-MoO_3 phase and only slight admixture of monoclinic β-MoO_3 phase was detected. But the content of β-MoO_3 in deposited evaporation products (powder) is significantly higher than in crystals.

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ФОРМИРОВАНИЕ КРИСТАЛЛОВ MoO_3 В ЭЛЕКТРОДУГОВОМ ИСТОЧНИКЕ ПЛАЗМЫ

А.В. Лебедь, А.Н. Веклич, В.Ф. Борецкий, О.Г. Колесник, С.П. Савенок, А.В. Андреев

Рассматривается формирование кристаллов триоксида молибдена при помощи электродугового разряда между молибденовыми электродами. Кристаллы формировались на боковой поверхности анода во время горения дуги. Эти кристаллы представляют собой прозрачные блестящие призмы и пластинки, состоящие, главным образом, из орторомбической фазы MoO_3. Для определения основных этапов формирования кристаллов, их химического состава и структуры применялись наблюдение зоны роста, рентгеноструктурный анализ, времяпролетная масс-спектрометрия и микроскопические исследования.

ФОРМУВАННЯ КРИСТАЛІВ MoO_3 В ЕЛЕКТРОДУГОВОМУ ДЖЕРЕЛІ ПЛАЗМИ

А.В. Лебідь, А.М. Веклич, В.Ф. Борецький, О.Г. Колесник, С.П. Савенок, О.В. Андрєєв

Розглянуто формування кристалів триоксиду молібдену за допомогою електродугового розряду між молібденовими електродами. Кристали формувались на боковій поверхні анода під час горіння вільноіснуючої електричної дуги. Ці кристали являли собою прозорі блискучі призми та пластинки, які складались, головним чином, із орторомбічної фази MoO_3. Для визначення основних етапів формування кристалів, їх хімічного складу та структури застосовувались спостереження зони росту, рентгеноструктурний аналіз, часопролітна лазерна мас-спектрометрія та мікроскопічні дослідження.