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SURFACE FORMATION OF MOLYBDENUM FOILS VIA ANODIZATION AND LASER IRRADIATION FOR CATALYTIC APPLICATIONS

MOLIBDEN FOLGALARNI ANODLASH VA LAZER NURLANISHI YORDAMIDA KATALIZDA QO'LLANILISHI UCHUN SIRTNI SHAKLLANTIRISH.

ФОРМИРОВАНИЕ ПОВЕРХНОСТИ МОЛИБДЕНОВОЙ ФОЛЬГИ ПУТЕМ АНОДИРОВАНИЯ И ЛАЗЕРНОГО ОБЛУЧЕНИЯ ДЛЯ ПРИМЕНЕНИЯ В КАТАЛИЗЕ

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Abstract

This study investigates the formation of developed surface modification of molybdenum foils through electrochemical anodization in oxalic acid and picosecond pulsed laser irradiation. The resulting surface morphology, elemental composition, and crystallinity were analysed using SEM, EDS, and XRD methods. Anodization process *produced a rough, none-uniform surfaces, while laser treatment achieved uniform micro-crystalline arrays. Advanced surface and micro-crystalline arrays by pulsed laser irradiation will open new ways in the field of catalytic applications.*

Annotatsiya

Ushbu ishda tadqiqot molibden folgalarning ustida rivojlangan sirt hosil qilish uchun oksalat kislotada elektrokimyoviy anodlash va pikosekundli impulsli lazer nurlanishi orqali amalga oshirildi. Natijada olingan sirt morfologiyasi, elementar tarkibi va kristallik SEM, EDS va XRD usullari yordamida tahlil qilindi. Anodlash jarayoni tartibsiz, notekis sirtlarni hosil bo'ldi, shuningdek lazer bilan ishlov berish orqali bir xil bo'lgan mikrokristallar massivlari hosil qilindi. Impulsli lazer nurlanishi orqali rivojlangan sirt va mikrokristallar massivlari kataliz sohasida qo'llanilish imkoniyatlarini ochadi.

Аннотация

Данная работа посвящена модификации поверхности молибденовой фольги посредством электрохимического анодирования в щавелевой кислоте и импульсной пикосекундной лазерной обработки для формирования развитой поверхности. Морфология поверхности, элементный состав и кристалличность были проанализированы с использованием методов СЭМ, ЭДС и рентгеновской дифракции. Процесс анодирования привела к образованию шероховатой, неоднородной поверхности, тогда как лазерная обработка позволила получить равномерные ряды микрокристаллов. Усовершенствованные поверхности и ряды микрокристаллов, полученные путем импульсного лазерного облучения, открывают новые перспективы в области применения в области катализа.

Keywords: *electrochemical anodization, picosecond laser, molybdenum foil, oxalic acid electrolyte, developed surfaces, surface morphology, composition.*

Kalit so'zlar: *elektrokimyoviy anodlash, pikosekundli lazer, molibden folga, oksalat kislota asosidagi elektroliti, rivojlangan sirt, morfologiya, tarkib.*

Ключевые слова: *электрохимическое анодирование, пикосекундный лазер, молибденовая фольга, электролит щавелевой кислоты, развитая поверхность, морфология поверхности, состав.*

INTRODUCTION

Over the past decades, there is found an increasing demand for energy which makes it a necessity for focusing on clean, low-cost, environmentally friendly, and renewable energy resources as population growth results in depleting fossil fuels, creates many environmental problems [1], [2]. This is due to the fact that catalytic reactions involving metal catalysts are a crucial component in the production technology of both inorganic and organic materials, as well as a key factor in the production of raw materials, significantly determining manufacturing capacity [3], [4]. However, increasing the molybdenum content in the coatings raises their internal stresses, leading to the formation of surface microcracks and reduced adhesion to the substrate [5], which probably reduces the stability of such electrodes and their effectiveness in the HER [6]. Additionally, defective coatings can be formed under the influence of molecular hydrogen at low pH and the formation of hydroxides at high pH. On the other hand, the catalytic activity of coatings with low molybdenum content can be enhanced by modifying their surface layers, particularly through anodic treatment, which has been applied to other systems [7]. This treatment increases the surface area of the electrode and develops a specific surface morphology with numerous active centres for HER, due to the etching of certain elements from the surface during anodic polarization [8]. However, in some cases, anodic treatment may result in the electrochemical polishing of the surface [5]. Therefore, when studying the catalytic properties of anodically treated Ni-Mo coatings for the hydrogen evolution reaction, it is essential to consider not only the surface morphology but also the influence of surface products on the hydrogen release mechanism, which depends on the parameters of anodic processes (potential, current density, duration). Laser ablation/irradiation is a green technique for obtaining nanoparticles of metal oxides, semiconductors and so on [9]. Herein, the oxygen-deficient MoOx NP films were synthesized through fairly simple programs of laser ablation and irradiation.

In this study, the electrochemical anodization of molybdenum foils in an oxalic acid electrolyte and pulsed laser irradiation comprised in order to develop surface layers suitable substrate microcrystalline arrays.

MATERIALS AND METHODS

Chemicals. Molybdenum foil 1÷3 mm thickness (99,9 % purity) and oxalic acid (99.6%) were purchased Fengda Chemicals Corporation China.

Anodizing process of molybdenum foil. The processes of liquid anodizing of molybdenum foil were carried out in a two-electrode chemical cell. Molybdenum foil served as working electrode (anode) while a graphite rod was used as the counter electrode (cathode). Prior to anodization surface of molybdenum foils were ultrasound cleaned in acetone, methanol and deionized water consistently in order to remove oil, dirt and other debris deposited from mechanical polished. After, cleaning, the metallic foil was dried in a muffle furnace for 3 hours at 100^0C. The experiment was started after surface treatment of initial metallic samples. In the first stage of anodization, the purified molybdenum metal foil was placed in an electrochemical cell containing 0.6 M oxalic acid ($C_2H_2O_4$) solution. The solution temperature was maintained at 5 ± 1^0C, while a voltage of 25÷40 V was applied for 360 minutes in galvanostatic mode. Following the initial anodizing stage that a uniform-rough, light-grey oxide film forms on the surface of the molybdenum substrate. The resulting sample was cleaned in distilled water.

Laser treatment of molybdenum foil. The surface treatment was performed using a PL2231-50 picosecond laser from EKSPLA with fundamental radiation at a wavelength of 1064 nm, a pulse duration of 28 ps, and a maximum pulse energy of 40 mJ. The sample under study was mounted on a holder in such a way that, after securing thin plates perpendicular to the laser beam axis, it could be moved along the X-Y-Z axes using micro-screws and stepper motors controlled by a computer program. Since the focal plane of the lens must be perpendicular to the beam axis and due to the dispersion of its material, the lens mount must also have micro-screws for translation and rotation along all three axes. In this case, the holder is equipped with guide rods that enable micro-movements along the three axes with a minimum step of 10 μm.

Characterization. A research-grade diode-pumped picosecond laser, model DPSS PL2231-50-SH/TH/FH, manufactured by EKSPLA (Lithuania). Morphological and elemental composition of anodized and laser irradiated samples was investigated using scanning electron microscopy (Zeiss EVO MA10) with Energy-dispersive X-ray spectroscopy (EDS). The XRD patterns was obtained using powder diffractometer PANalytical Empyrean diffractometer (CuKα-radiation). Surface microstructure of the samples was carried out using Axio Scope (AXIO) optical microscopy with a built-in AXIOCam ERc5S digital camera.

RESULTS AND DISCUSSION

In Figure 1 (a,b) schematic illustrated electrochemical anodizing process of molybdenum foil in liquid medium. Specifically, the metal foil was mounted horizontally on the back side of a Teflon beaker, sealed with a rubber and a molybdenum platform as shown in Figure 1 (a). Thus Figure 1 (b) shows that the changing of voltage during anodizing proses in three sections of voltage distribution. It shows voltage dependence from anodization time. In particular, the evolution of voltage during anodization time, the voltage increased (section I) and reach maximum (section II). Then voltage start decrease (section III) and become constant as presented as a solid line in Figure 1 (b). Accordingly, decreasing voltage shown that in section III can be attributed formation of none uniform roughness on molybdenum surface. Figure 1 (c) shows that surface morphology and elements identification of initial sample before anodizing that measured by SEM and optical microscopy. According to the images of SEM, the surface of the cleaned molybdenum foil is uniform. The formation of roughness occurs in an aqueous solution of oxalic acid by an electrochemical method. The concentration and purification of the electrolyte, the temperature of the anodizing process and the applied voltage are critical parameters in the anodizing of molybdenum foil. Figure 1 (d) show XRD pattern of the initial molybdenum foil, as depicted in the provided image, shows a spectrum with counts plotted against the 2θ position. The pattern indicates the presence of molybdenum as the primary element, with a dominant peak at approximately $58\text{-}60^0$, corresponding to the characteristic diffraction of molybdenum's crystalline structure. This peak is sharp and intense, suggesting a high degree of crystallinity and a well-ordered lattice. In spite of metallic surface of the sample polished and cleaned by ultrasound, but at the same time had small residual strips of rolled metal. There are small longitudinal strips are observed on surface (before polishing) caused by rotation, elongation and pressure of the rolling shafts that shown in Figure 1 (e). In general, the morphology of the sample is identical over the entire surface. Local elemental analysis of the surface of the samples shown in Figure 1 (c). It was observed that following ratio of the starting components consist from molybdenum having an atomic weight of up to 87 percent, while the oxygen content reaches up to 13 atomic percent Figure 1 (c).

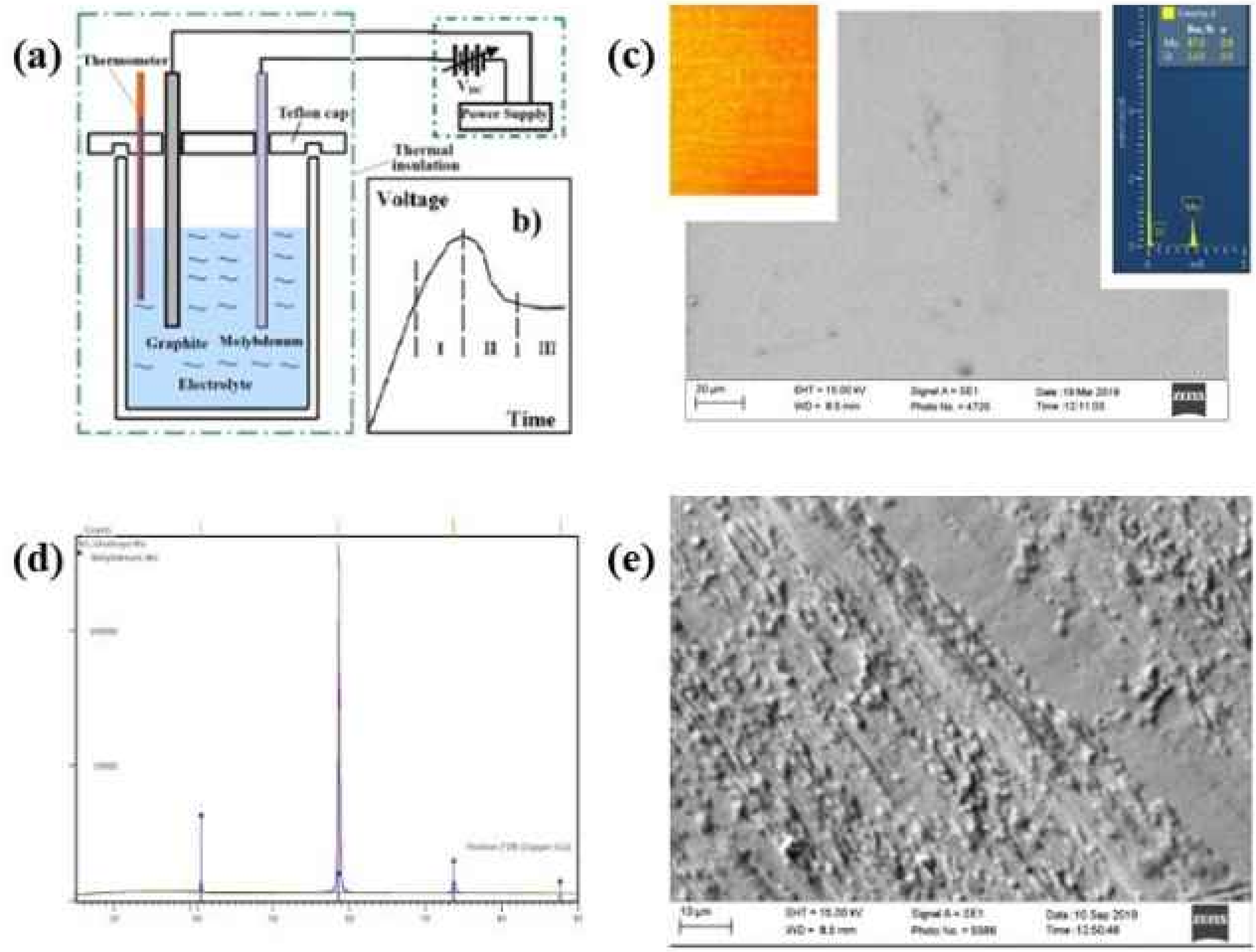

Figure 1. (a) view of experimental setup for anodization; (b) the evolution of voltage during process anodization; (c) SEM image and EDS composition (top left side) and optical microscopy image (top right side) of initial molybdenum surface after mechanical polishing and cleaning; (d)XRD of initial molybdenum foil, (e) magnificated SEM images.

Then after anodizing process for 360 minutes in a solution of 0.6 M oxalic acid, the temperature of which was maintained in the range from 5 ± 1^{0}C, the randomly oriented roughness is observed on sample surface of molybdenum foil in Figure 2 (a). A comparative analysis shows that the surface of the sample is covered with non-uniform roughness, micropores are visible that are heterogeneous in shape and size that are randomly located and have a large spread on the surface. Increasing image magnification up to 2 µm scale in Figure 2 (b) shows that on the anodized molybdenum surface formed non-uniform roughness, one arrangement was very irregular with wide range of size distribution. The investigation of surface morphology also revealed that non-uniform flecks inhomogeneity with different diameters distributed over all anodized surface of molybdenum foil with constant anodizing voltage. In addition, Figure 2(b) shows composition of anodized molybdenum foil on the upper right corner. According to EDS spectrum the main part is molybdenum having an atomic weight of up to 96,7 percent, while the oxygen content reaches up to 3,3 atomic percent on the upper right corner in Figure 2 (b).

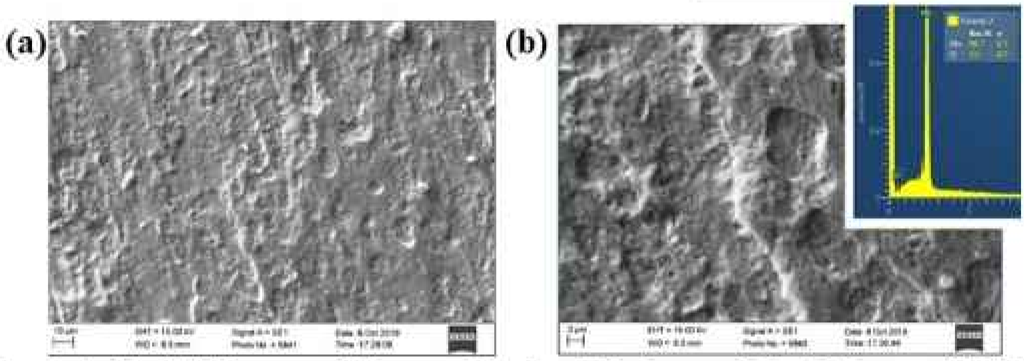

Figure 2. (a) SEM image of the anodized molybdenum foil at 6 hours; (b) high magnification SEM image and the elemental composition of anodized sample shown on the upper right corner.

In order to prevent intense laser ablation resulting in hole formation, a surface modification mode of molybdenum foil was used with pulsed laser irradiation at a wavelength of 266 nm, where the maximum pulse energy was 0.6 mJ, the repetition rate was 50 Hz, the sample movement speed was 30 mm/min, and the interval between lines was 50 μm. Using this mode, the movement of the sample holder was programmed to guide the laser beam in a pattern of continuous horizontal, vertical, and diagonal lines at a sample movement speed of 30 mm/min on the surface of metal foil that shown in Figure 3 (a). The surface heating process is of interest for creating uniform micro-crystallites arrays on the metal surface. If the metal surface is irradiated with a laser beam in the pattern shown in Figure 3 (a), we observed that uniform micro-crystallites arrays will form on the metal surface. The SEM image Figure 3 (b) shows a comparative view of two surfaces of molybdenum foil border with picosecond laser-treated surface and an untreated area. The left side of the image displays a highly structured surface with a uniform structure. The texture of surface indicating the formation of microcrystalline arrays due to the laser irradiation. The pattern is consistent and evenly distributed, suggesting precise control during the laser treatment process. The contrast between the two surfaces highlights the significant impact of picosecond laser irradiation, transforming the initially smooth molybdenum foil into a structured, developed surface with formation of microcrystalline arrays in all molybdenum surface see Figure 3 (c)

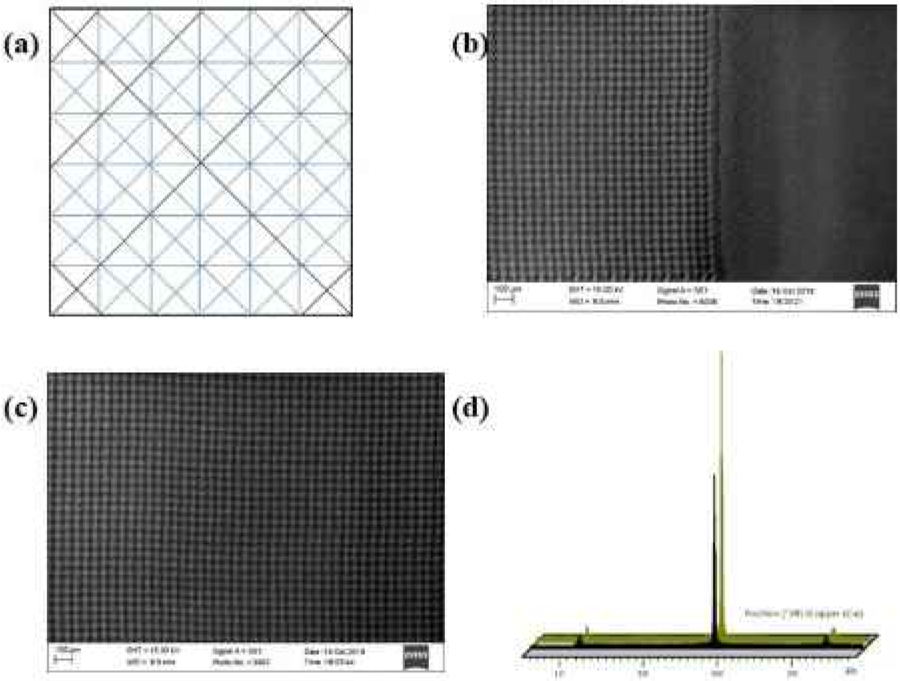

Figure 3. (a) pattern of continuous sample movement; (b) SEM images of the border and (c) full molybdenum foil surface; (d) XRD pattern before and after treated by picosecond laser.

Figure 3 (d) presents the XRD patterns of initial molybdenum foil and after treated by laser irradiation. The XRD patterns were analyzed using the HighScore software and compared with the PDF-2 database (2013 edition). The peaks are relatively sharp and well-defined suggesting a high degree of crystallinity and a uniform structure. The diffraction peaks are sharp and narrow, indicating a high degree of crystallinity metallic molybdenum phases of initial molybdenum foil. The XRD patterns exhibit notable increasing of peak intensities after pulse laser irradiation.

CONCLUSIONS

This paper presents studies of the processes of anodizing in the oxalic acid electrolyte of molybdenum foil. In this case, anodizing conditions were selected in order to observe visible uniform roughness. After completing electrochemical anodization of molybdenum foil is covered with non-uniform roughness, micropores are visible that are heterogeneous in shape and size that are randomly located and have a large spread on the surface. However, in order to receive highly ordered micro-crystalline arrays on the surface of molybdenum foil, it is treated by picosecond laser irradiation with pulse energy 0.6 mJ, the repetition rate 50 Hz, foil movement speed 30 mm/min in the form of continuously horizontal, vertical, and diagonal lines. After that uniform micro-crystallites arrays were obtained on the molybdenum foil surface. X-ray patterns and EDS analysis were identified absence of other impurities of the structure of molybdenum. In conclusion the comprising anodized and laser treated sample lead to formation different microstructure of surface. But laser treatment stimulated to formation highly ordered micro- crystalline developed surface.

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