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On the tungsten single crystal coatings achieved by chemical vapor transportation deposition

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ABSTRACT

The tungsten single crystal has many excellent properties, namely a high melting point, high anti-creeping strength. Chemical vapor transportation deposition (CVTD) is a possible approach to achieve large-sized W single crystals for high-temperature application such as the cathode of a thermionic energy converter. In this work, CVTD W coatings were deposited on the monocrystalline molybdenum substrate (a tube with <111> axial crystalline orientation) using WCl_6 as a transport medium. The microstructures of the coatings were investigated by a scanning electron microscope (SEM) and electron backscatter diffraction (EBSD). The as-deposited coatings are hexagonal prisms—rough surfaces perpendicular to <110> with alternating hill-like bulges and pits at the side edges of the prisms, and flat surfaces perpendicular to <112> with arc-shaped terraces at the side faces. This can be explained by two-dimensional nucleation -mediated lateral growth model. Some parts of the coatings contain hillocks of an exotic morphology (noted as "abnormal growth"). The authors hypothesize that the abnormal growth is likely caused by the defects of the Mo substrate, which facilitate W nucleation sites, cause orientation difference, and may even form boundaries in the coatings. A dislocation density of 10^6 to 10^7 (counts/cm^2) was revealed by an etch-pit method and synchrotron X-ray diffraction. As the depositing temperature rises, the dislocation density decreases, and no sub-boundaries are found on samples deposited over 1300 °C, as a result of atom diffusion and dislocation climbing.

1. Introduction

Serving as a power source in satellites and space stations, thermionic reactors have several advantages over solar arrays commonly utilized in spacecraft, including a simple but stable structure with no rotating components, the possibility of miniaturization, utility in the dark, and a higher power density during constant high-power output [1,2]. Nevertheless, the cathode of the thermionic energy converter, which is the "heart" of the reactor, must operate at a high ambient temperature of about 1500 °C throughout the service period. The tungsten single crystal has a combination of many excellent properties including a high melting point, high anti-creeping strength, high elastic modulus, high resistance to radiation, and a good thermionic emission work function [3,4]. These make W single crystals an ideal material for the functional layers of the cathode. The microstructures of the single crystal significantly affect the lifespan and stability of the W functional layers. This is especially true when the crystal consists of many sub-grains [5]. Thus, this investigation into microstructures is important. In previous studies, electron beam floating zone melting (EBFZM) can produce bulk single crystals of high-purity W, but not W single crystal coatings [6,7]. Conventional chemical vapor deposition (CVD) of W single crystal coatings has been reported as well. Researchers have deposited thin films of W single crystals on Si and Cu substrates using $W(CO)_6$ as a precursor, but the film contains impurity elements (C and O) [8–10]. Researchers of Auburn University and Uppsala University have used laser chemical vapor deposition to grow micron-sized tungsten single crystals from a reaction gas mixture of WF_6 and H_2 [11]. Moreover, these CVD methods usually have challenges in the preparation of large-sized W single crystal coatings—this limits the application of these methods. Chemical vapor transportation deposition (CVTD) is an emerging method for obtaining W single crystals. Achieving W single crystals by CVTD has made some substantial developments [12]. In our previous work, we have studied the CVTD of W on the molybdenum substrate using WCl_6 as a transport medium, the proportion quantitative analysis and etching of the {110} planes of the as-deposited W coatings [13–15].

Here, we studied the growth habit, abnormal growth, and defects (dislocations and sub-boundaries) of the W coatings grown by CVTD. The growth habit was revealed based on the W coatings' morphology.

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Table 1
Physical properties of W and Mo.

Material	Melting point (°C)	Density (g/cm^3)	Thermal conductivity (cal/(cm·s·°C))	Coefficient of expansion (10^{-6}/°C)	Lattice constant (Å)
Mo	2625	10.22	0.340	4.9	3.14
W	3410	19.30	0.397	4.6	3.16

The abnormal growth on the surface of the W coatings was investigated by scanning electron microscope (SEM) and electronic backscatter diffraction (EBSD). We discuss a possible explanation for the abnormal growth. The dislocations and sub-boundaries in the coatings were studied via an etch-pit method and synchrotron X-ray diffraction.

2. Materials and Experimental

In this work, W coatings were fabricated by CVTD. A polycrystalline W tube of high purity (total impurity content is 0.0052 wt%) was used as the source of W, and WCl_6 of high purity (over 99.99%) was used as the transport medium of W. The monocrystalline Mo tube with <111> crystalline orientation (crystal axial declination angle <3°) was fabricated by the Northwest Institute for Non-ferrous Metal Research using electron beam floating zone melting (EBFZM). Its dislocation density was as high as 10^6 (counts/cm^2). The Mo tube (with the appearance of sub-boundaries) served as a substrate for the deposition of W. Mo and W have similar linear expansion coefficients and a body-centered cubic space lattice with similar lattice constants (see Table 1). Thus, cracks and thermal deformation are not likely to happen when heated—the lattice mismatch is relatively low (only 0.633%). Three W coatings were prepared under different substrate temperatures. Sample W_{1300} was deposited at 1300 °C. Sample $W_{1300–1400}$ was first deposited at 1300 °C for 20 min and then heated to 1400 °C, and W_{1400} was deposited at 1400 °C. The pressure of the reaction chamber was 15.77 Pa, the temperature of the W source was kept at 360 °C below the substrate temperature, and the temperature of the evaporating chamber was 120 °C.

The coatings were examined by the unaided eye and SEM (JEOL JSM-7001F thermal field emission SEM). The crystal orientations of different W coating surfaces were analyzed by EBSD (JEOL JSM-7001F thermal field emission SEM, with Data Collection 5 software developed by EDAX). The sample was placed in the sample chamber of the SEM. It was inclined at a large angle of 65°–70°. The CCD camera captured the Kikuchi pattern generated by electron diffraction. This was automatically analyzed by computer, after which the software generated an EBSD grain orientation map.

Although transmission electron microscope (TEM) can resolve the detail of the dislocations and other defects in the crystal, it can only observe an extremely small area each time. Rather, we used an etch-pit method in which the density of the etch-pits represents the density of the dislocations to investigate the coatings [16]. The lattice distortion caused by the presence of a dislocation allows foreign atoms to accumulate and results in a relatively higher energy state in the atoms adjacent to the dislocation. The dislocation outcrop is therefore more easily attacked due to foreign atoms and the higher energy state. It makes the etch-pit visible with microscopy under appropriate etching conditions. After repeated experiments, we found a feasible etchant that used a solution of 10 g NaOH and 10 g $K_3Fe(CN)_6$ dissolved in 80 ml deionized water. The etch-pits obtained could be well distinguished and facilitated automatic computer-based analysis of dislocation density. After being ground by abrasive paper and polished to a fine finish, the W coatings were etched and observed under an optical microscope (OM, OLYMPUS BX51M). The OLYCIA M3—a metal analysis software—was used to calculate the dislocation density of the samples.

Fig. 1 shows three typical types of different etch-pit morphologies etched by the etchant mentioned above. As shown in the figure, the etch-pit of the {110} planes are an incomplete rhombus (Fig. 1a). For the {112} planes, it is an irregular quadrilateral (Fig. 1b). For the {111} planes, it is an equilateral triangle (Fig. 1c).

The formation of different etch-pit morphologies can be explained by the following theory. The W has a BCC structure and the close-packed {110} planes show the lowest surface energy [17,18]. After etching, the {110} planes will eventually be exposed to show intersections of the surface planes and {110} planes form the shapes of these etch-pits. According to the zone law, let R_i be the vector of the intersection of plane H and plane A_i. Then, $R_i = H \times A_i$. And let φ_{ij} be the angle between R_i and R_j, and then $\cos\theta_{ij} = (R_i \cdot R_j)/(|R_i| \cdot |R_j|)$. Take the (111) plane for example.

$$R_{(110)} = [111] \times [110] = \begin{bmatrix} i & j & k \\ 1 & 1 & 1 \\ 1 & 1 & 0 \end{bmatrix} = [\bar{1}10]$$

By applying the same mathematical technique, we can show that the intersections of the (111) surface plane and the {110} plane family are $[\bar{1}10, 10\bar{1}, 0\bar{1}1, \bar{1}\bar{1}2, \bar{1}2\bar{1}]$ and $[2\bar{1}\bar{1}]$. The angles between them are 30°, 60°, 90°, 120° and 150°. Thus, we can obtain a geometric model of the etch-pit of (111) (shown in Fig. 2a). It is the same for the (112) plane (see Fig. 2b) and the (110) plane.

To further determine the dislocation density, the samples were investigated by synchronization radiation X-ray produced by the Advanced Photon Source (APS) in the II-ID-C high energy X-ray research station of the Argonne National Laboratory. The sample was fixed on the sample platform for rotation or swinging. A beam of high energy X-rays was introduced into the station through a beryllium window—this was restricted by a slit that can determine the size of diffraction spots and irradiate the sample. The pattern

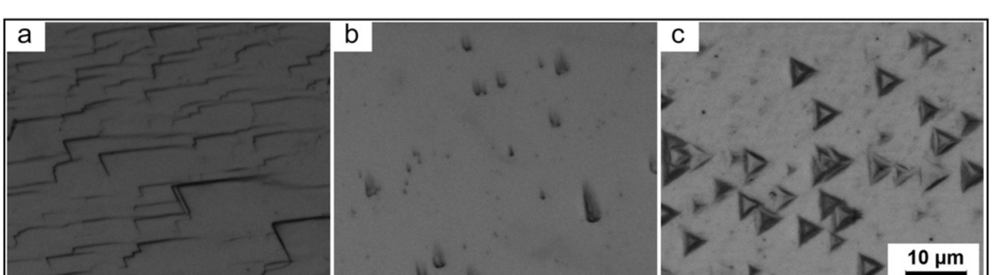

Fig. 1. Three typical types of different etch-pit morphologies, (a) {110}, (b) {112} and (c) {111}.