



The crystallographic structure of the air-grown oxide on depleted uranium metal



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ABSTRACT

Oxide formation on depleted uranium metal was investigated using a combination of electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM) characterisation. Diffraction analysis of the oxide revealed an FCC crystalline formation of UO₂ crystallites whilst TEM data indicated an average grain size of 12 nm with a standard deviation of 3.8 nm. EBSD analysis revealed a preferential texture of [110] normal to the surface of the metal. This data implied that lattice matching between the oxide and the underlying metal did not occur, therefore, the observed preferential growth direction is independent of the underlying crystal orientation.

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1. Introduction

Understanding the factors which influence uranium corrosion is of relevance to a variety of industrial, environmental and academic activities. Of particular interest is the behaviour of uranium within long-term storage and disposal environments, i.e. in the presence of atmospheric gasses such as oxygen and water vapour.

A particular concern regarding the corrosion of uranium in humid environments is that when this occurs in a sealed container the reaction will consume oxygen [1]. If the oxygen level is sufficiently reduced then the water–uranium reaction produces hydrogen, thus potentially forming pyrophoric uranium hydride. However, the initiation of uranium hydride reaction sites has been shown to be strongly dependent on the characteristics (e.g. thickness) of the surface uranium oxide layer present on the uranium metal [2–6].

The clear influence that the uranium surface oxide layer has on hydride site initiation has led to the development of mathematical models which assume that site nucleation is controlled by the transport of hydrogen through the oxide to the underlying metal. The model put forward by Ben Eliyahu et al. [7] assumes

that hydride reaction sites are limited to a maximum concentration for a given uranium surface. In contrast, Glascott proposed a model in which there is a distribution of oxide layer thickness across the uranium surface which leads to a variation in the observed number of hydride reaction sites with time [8].

It is, therefore, evident that characterisation of the air grown surface oxide layer on uranium (i.e. crystallite size and orientation) would further the mechanistic understanding of uranium corrosion, both in relation to the reaction with moist air and also with hydrogen.

The rate and mechanism of the reaction of uranium with oxygen and water has been studied with each gas in isolation and also for mixtures of the two gasses [2,9–21]. These investigations utilised techniques such as gas consumption [9], mass gain analysis [13,15], ellipsometry measurements [10,17,18], Raman spectroscopy [19], X-ray photoelectron spectroscopy [20] and infra red spectroscopy [21]. Thus, few studies have been reported regarding the characterisation of the structure of air-grown uranium oxide film on a sub- μm scale.

However, an early X-ray diffraction (XRD) study by Waber et al. [22] reported that uranium dioxide formed by the reaction of uranium with water vapour occurs with a distinctive growth habit. The (110) planes of the dioxide were reported to lie parallel to the surface of the uranium substrate. Furthermore, no evidence was found for an epitaxial relationship between the metal and the oxide.

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A subsequent XRD and electron diffraction study carried out by, Bessonov et al. [23] concluded that the oxide film formed on uranium samples by air exposure at room temperature was UO_2 , with a lattice parameter $a = 0.545$ nm. Furthermore, the oxide was stated as having a polycrystalline structure with broadening of the XRD spectra indicating a crystallite size of approximately 10^{-4} cm (i.e. ~ 1 μm). Similar XRD measurements have since been reported by Chernia [21], giving an oxide crystallite size of 15 nm for a 270 nm thick oxide grown at 160 °C in oxygen. Furthermore, an oxygen-anion hopping mechanism was proposed to account for the observed preferred growth in the [110] direction.

Theoretical work by Tasker [24] calculated the surface energy, tension and structure of the low index faces of uranium dioxide using an ionic description of the crystal formation. The (111) orientation exhibited the lowest surface energy, however, the individual planes are charged since they consist of only one ion type (either uranium or oxygen). Whilst for the (110) orientation the surface energy is higher but individual planes of atoms are charge neutral, consisting of a mix of uranium and oxygen atoms making this the favourable growth direction.

From the discussion presented above it is clear that no direct observations have been reported of the microstructural configuration of uranium oxide forming on metal surfaces. Therefore the current work utilised focused ion beam (FIB) to prepare cross-sections through the surface of deliberately oxidised samples. Transmission electron microscopy (TEM), scanning TEM (STEM) and scanning electron microscopy (SEM) methods were employed to directly image the oxide layer to determine crystallite size. In addition, TEM and electron backscatter diffraction (EBSD) provided complimentary data by confirming the crystalline structure and orientation of the oxide overlayer. Particular attention was devoted to identifying a relationship, or lack thereof, between the crystal orientation of the exposed metal surface and the growth direction of the formed oxide layer.

2. Experimental method

2.1. Initial surface preparation and oxidation

The current study utilised two types of depleted uranium samples, referred to as low carbon (<100 ppm) and high carbon (600 ppm). The low carbon samples were identical to those used in a previous study [25], i.e. 10 mm \times 10 mm, ~ 1 mm thick, with a grain size of ~ 15 μm . Chemical analysis of samples from the same source yielded impurity levels for iron, aluminium, silicon and chromium of 22, ~ 5 , ~ 2 and ~ 2 ppm (by weight), respectively [6]. These samples were obtained from rolled feedstock and annealed for 164 h, at 550 °C under vacuum at $< 1 \times 10^{-4}$ Pa, prior to further preparation.

The high carbon samples were in the form of disks (15 mm diameter, 1 mm thick) cut from a cast rod. These samples were identical to those used in a previous studies [26,27]. In general, higher impurity levels were present within the high-carbon samples as compared to the low-carbon samples, with analysis of material from the same source as the high-carbon samples indicating levels for iron, aluminium, silicon and chromium of ~ 140 , ~ 40 , ~ 130 and ~ 20 ppm (by weight) respectively [28]. Prior analysis of the microstructure of the samples indicated a coarsely grained texture typical of cast metal, with large grains frequently > 100 μm in width, with long, relatively straight, low angle ($< 25^\circ$) grain boundaries and occasional sets of well defined crystal twins.

In each instance the metal coupon surfaces were prepared in the open laboratory using wet mechanical polishing. Samples were abraded using water as a lubricant on Buehler SiC paper of increasingly fine grade (from P600 to P2500) in a process designed to minimise the work hardening effect on the bulk metal. The

surfaces were then lapped using a 1 μm diamond paste on a short nap cloth, then rinsed in ethanol and dried in air.

Controlled surface oxidation was performed upon two coupons (one of each purity) in the open laboratory at room temperature and pressure for a duration of 42 days, the oxides formed in this manner were the primary focus of the TEM investigation. In order to form a substantial oxide layer several microns in thickness, four coupons (two samples of each purity) were oxidised in a conventional oven for 12 h at 150 °C. One low carbon and one high carbon sample were then retained for TEM/STEM analysis while the remaining samples were prepared for EBSD analysis.

2.2. Sample preparation for TEM analysis

In situ TEM sections were prepared from both purities of uranium metal following oxide growth at room temperature and 150 °C. A platinum coating was deposited prior to ion beam milling, in order to protect the oxide surface. A Helios X600 Dualbeam system was used to cut $10 \times 5 \times 1$ μm sections of material from the surface, and a kleindike nanomanipulator needle was used to extract the cut sections. After controlled ion beam milling to form a TEM section 1 μm thick, the nanomanipulator needle was attached via further controlled platinum deposition and the section was cut and lifted free. Once removed, the 1 μm thick slice was positioned over a half-moon shaped TEM grid and attached using platinum deposition. The sample was then thinned, in situ, to a thickness of 50–100 nm and following STEM imaging at 30 kV transferred to the TEM system. TEM analysis of samples was performed on a Jeol 2010 transmission electron microscope; for image and diffraction pattern collection a Gatan Orius SC 1000 camera was used. Spot diffraction was obtained at 300 \times magnification with a 1 nA probe current, a 2 s dwell time and a 200 nm selected area aperture.

2.3. Sample preparation for EBSD analysis

EBSD analysis currently requires a minimum grain size of 50 nm in order to produce measurable kikuchi bands for computational analysis. Therefore, samples with the thick oxide layer (> 5 μm) formed at 150 °C were heated to 550 °C under UHV conditions for 12 h in order to anneal the sample and induce grain growth. The annealed microstructure will therefore differ from an ambient formed oxide, however, in terms of crystallographic orientation, the annealed oxide is likely to be sufficiently representative of the air grown oxide to determine if there exists a preferred crystal orientation in relation to the underlying parent metal grains.

The annealed samples were loaded into an FEI FIB201 focused gallium ion beam instrument for grazing-angle etching, producing a section through both the oxide and the underlying metal. Samples were ion etched at a 10° angle parallel to the surface, at the maximum probe current of 11.5 nA, to produce a surface suitable for EBSD mapping. A shallow etching angle is required to produce surface architecture that would allow diffracted electrons to reach the detector. An additional benefit of utilising an acute angle through the oxide (as opposed to etching to the surface normal) is an increase in the surface area of exposed oxide available to be mapped.

After preparation in the FIB, the samples were transferred into a Zeiss EVO MA10 equipped with LaB_6 electron source and TSL-EDAX instrumentation, for crystallographic electron backscatter diffraction mapping (EBSD) of the etched areas. EBSD data were recorded using OIMTM software for both data capture and analysis. The metal was mapped using structural data provided from the standard TSL database for orthorhombic α -uranium, whilst the oxide was mapped using the structural data for UO_2 . Where necessary, the raw EBSD data recorded during mapping runs were cleaned using

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