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SURFACE EXTENDED X-RAY ABSORPTION FINE STRUCTURE APPLIED TO THE POLYCRYSTALLINE SURFACES OF REAL THERMIONIC CATHODES


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Abstract

We have used Surface Extended X-ray Absorption Fine Structure (SEXAFS) to study the local geometry around barium atoms on thermionic emitting cathodes at their normal operating temperatures. On the surfaces of tungsten and tungsten/osmium alloy dispenser cathodes Ba is bonded to oxygen with a well-defined short-range order. The Ba-O distance is almost the same for both cathodes, but the alloy cathode has Ba bonded to two oxygen near neighbours (compared to one for the tungsten cathode), which lie in hollow sites of the substrate. This provides an explanation of the lower work function observed for the alloy cathode.

Introduction

SEXAFS has proved to be the best method for precise determination of the structure of adsorbates on surfaces [1]. Here we describe an extension of the technique into a new area of application: the geometry of a surface complex on a polycrystalline substrate. In this study the bond lengths and orientation have been determined for the barium-oxygen-substrate complex on the surfaces of real thermionic dispenser cathodes [2].

Thermionic cathodes are important practical devices, being widely used in applications needing high electron current densities, such as klystrons and cathode ray tubes. The dispenser cathode is constructed from a porous matrix of polycrystalline tungsten, impregnated with barium calcium aluminate, surrounding an internal filament. In the operating temperature range of 1100 to 1400 K, the impregnant dissociates and a mixture of Ba and BaO diffuses through the pores between the tungsten crystallites and across the surface. This forms a low work function coating which is in dynamic equilibrium with the barium-containing evaporants being thermally desorbed from the surface. The performance of dispenser cathodes has been improved by coating the surface with third-row transition metals or their tungsten alloys [2]. Re, Os and Ir are the best such metals at reducing the work function (y) of the cathode, a reduction of up to 0.2eV being achieved; Pt and Au are notably bad, with W-Pt coated 'cathodes' having a work function 0.2 eV higher than a pure W matrix cathode.

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It is known [21] that the low-\(\phi\) coating is less than a monolayer, and that the principal constituents of the active layer are barium, oxygen and tungsten. However, the details of the bonding and the orientation of the Ba-O-W complex have not been fully understood, largely because the surface structure has no long range order, thus precluding study by low energy electron diffraction (LEED) or other diffraction techniques. This is where SEXAFS holds a major advantage, since it probes only the local structure around adsorbate atoms, and is thus the technique of choice for studying disordered and polycrystalline surface phases.

Experiment and Results

Our samples were real dispenser cathodes, manufactured in the usual way, and differing from commerical devices only in being polished to give a flatter surface. They were chosen to be representative of the best uncoated W matrix cathodes (B-type), an improved alloy-coated cathode (CD-type), and a 'cathode' with poor emission characteristics (W-Pt alloy). The emission characteristics and Auger electron spectra (AES) of the cathodes were checked before and after the SEXAFS measurements, and found to be indistinguishable from those obtained from batches of normal cathodes.

Surface EXAFS spectra were measured using apparatus [3] at the Daresbury Laboratory Synchrotron Radiation Source, with the absorption coefficient above the Ba L\(_2\)-edge at around 5247 eV being recorded by collecting the total electron yield in a Faraday cup detector placed close to the sample. The best quality SEXAFS data were collected with the cathodes at room temperature, but a significant number of the SEXAFS measurements were performed with the samples at temperatures between 825 and 880°C, where they are actually working as good cathodes, emitting about 1 Amp of electrons. The cathodes were biased to suppress this, so that the detector received only the current due to photon absorption. Careful comparison of many spectra from all of the samples in our study showed that the same frequency components were reproducibly present in the SEXAFS data from hot and cold cathodes, indicating that the surface complex involving the barium atoms has the same basic local structure at both temperatures.

The data were analysed, after the usual background subtraction and conversion to \(k\)-space, by a curve fitting routine based on the rapid curved wave computational scheme [4], including a least squares iteration to give the best theoretical fit to the experimental data. Electron scattering phase shifts for Ba, O and W were calculated using a "muffin tin" potential-based method, and checked against our measured EXAFS spectra from BaO (prepared in vacuo by thermal decomposition of BaCO\(_3\) on a Pt substrate), Ba\(_2\)O\(_3\), BaMoO\(_4\) and samples of the impregnant compound.

The coordination numbers and bond lengths derived from our SEXAFS analysis are presented in Table 1. The experimental noise level prevents observation of shells at greater distances than about 4.5 \(\AA\). The error bars on the distances (arising mainly from random statistical fluctuations between successive runs) are somewhat worse than those attainable with state-of-the-art SEXAFS on well-defined single crystal surfaces. Although the EXAFS technique is not particularly good at discriminating between different types of neighbour atoms, in this case the distinctly different backscattering signatures for Ba, oxygen and the substrate metal readily allow us to determine which atoms are involved in each shell of neighbours (although the small differences between W, O\(_s\) and Pt cannot be distinguished). It can thus be stated that the Ba atoms are coordinated directly to oxygen, with substrate atoms as next nearest neighbours, for both types of good cathode studied here. Such surface structural information has not previously been obtained on real cathodes, and indeed it was not even known whether there was a unique, well-defined Ba-0-W surface complex.

The same samples used in these measurements were also analysed by X-ray diffraction (XRD) in a grazing incidence geometry to emphasise the contribution of substrate planes near to the surface. For the B-type cathode (pure W matrix), a b.c.c. diffraction pattern was obtained which indicated a slight preponderance of a number of crystal planes parallel to the surface. The CD-type (W/Os alloy) cathode was found to be mainly h.c.p., as might be expected from the bulk phase diagram for W/Os, \{10\(\bar{1}\)0\} planes dominating the surface contribution to the XRD pattern. For the Pt/W alloy cathode, the surface was found to almost entirely consist of platinum (f.c.c.) \{111\} planes.
Table 1. Nearest and next-nearest neighbour distances (R, A) and coordination numbers (N) derived by SEXAFS for Ba atoms on the surfaces of three types of thermionic dispenser cathode.

<table>
<thead>
<tr>
<th>Cathode type</th>
<th>Nearest neighbour (Ba-O)</th>
<th>Next nearest neighbour (Ba-W)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R (±0.04 A)</td>
<td>N (±0.5)</td>
</tr>
<tr>
<td>B (W matrix)</td>
<td>2.62</td>
<td>1</td>
</tr>
<tr>
<td>CD(W/Os alloy)</td>
<td>2.61</td>
<td>2</td>
</tr>
<tr>
<td>W/Pt alloy</td>
<td>2.72</td>
<td>1</td>
</tr>
</tbody>
</table>

(a) the technique cannot distinguish between W, Os and Pt neighbours
(b) No well-defined Ba-metal distance was observed for this surface.

Discussion
To deduce surface structural models for the cathodes, we combine information on local structure (SEXAFS), the predominant morphology (XRD), surface composition (AES) and work function. Φ can be related semi-quantitatively to the dipole strength of the oriented Ba-O surface layer, this dipole strength depending on the ionicity of the Ba and O via the well-known Helmholtz relationship. The observed work functions can therefore be used to estimate the appropriate Ba and O ionicities and hence their atomic radii [5].

Numerous models of Ba-O-W surface complexes on the exposed crystal planes of the cathodes were considered. For the B-type and CD-type cathodes, the results of our modelling exercise strongly favour surface complexes of the type shown in Fig. 1. Similar structures can be derived for all crystal planes present in significant proportions at the B-type cathode surface.

![Fig. 1 The surface complexes derived for (a) a {1010} face of the W/Os alloy (CD-type) and (b) a {211} face of the W matrix (B-type) cathodes. The Ba atoms are depicted as white, O atoms grey and substrate atoms black, with no distinction being made in this model between the W, Os and Pt substrate atoms. The choice of atomic radii is described in the text.](image)

We propose that the morphology of the surface plays an important role in determining the efficiency of cathodes. The more open structure of the CD-type surface planes has a Ba atom bridging two O atoms. This will result in greater electron transfer towards the surface, a larger surface dipole, and a smaller work function. In addition, an open structure allows the O atoms to sit in the surface layer, below the Ba atom (this orientation is also consistent with our angularly-resolved AES measurements). In this configuration, electron transfer from the oxygen end of the Ba-O adsorbate into the surface should be maximised,
increasing the surface dipole. By the same argument, charge transfer from Ba-O to the close packed surface of the W/Pt alloy will be minimised. There may thus be an optimum surface crystallography which could hold the key to development of even more efficient cathodes.

References