NEW CATHODE EMISSION MATERIALS FOR HIGH PRESSURE SODIUM LAMPS

PhD Thesis

ILDIKÓ BECK

SUPERVISORS:

VARGÁNÉ DR. JOSEPOVITS, KATALIN, ASSISTANT PROFESSOR
BME, FACULTY OF NATURAL SCIENCES, DEPARTMENT OF ATOMIC PHYSICS, PHYSICAL INSTITUTE

DR. SNEIDER, JÁNOS, CI SYSTEM MANAGER
GE CONSUMER & INDUSTRIAL, TUNGSRAM

DR. POKOL, GYÖRGY, PROFESSOR
BME, FACULTY OF CHEMICAL AND BIOENGINEERING, DEPARTMENT OF GENERAL AND ANALYTICAL CHEMISTRY

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SCOPE OF THE STUDY AND EXPERIMENTAL

The manufacturing of the High Pressure Sodium (HPS) lamps became significant with the development of the arc tube a half-century ago. The arc tube is made exclusively from ceramic based material to resist high pressures over 10000 Pa, high temperatures (2500 ºC) that take place during operation and aggressive Na vapor. Originally this type of lamp was only used as an outside light source.

Inside the ceramic tube, an arc discharge is initiated between two tungsten electrodes. Due to their high temperature, the electrons leave the tip of the electrodes by thermionic emission. In order to achieve a lower work function and thus higher light flux, the surface of tungsten cathodes are covered with Ba containing rare earth and alkali earth tungstate emission material. The surface covering is produced by sintering mixtures such as BaCO₃ (as a source of BaO), Y₂O₃ or Sc₂O₃ and WO₃, in stochiometric quantities. The emission material vaporizes by a dissociative process at high operating temperature as a result of the reaction with the polycrystalline tungsten cathode, generating free Ba at the surface. This Ba (BaO) coverage creates an improved lamp performance by lowering the electron work function ($\Phi$) of the tungsten electrodes and the operating temperature.

The operation mechanism of the cathodes is based on the formation of a Ba-O double-layer, which is a widely investigated area along with Ba diffusion from the seventies. Many efforts have been taken to understand the mechanism of thermionic cathodes and to comprehend if a homogenous or partial Ba layer evolves during operation time of the cathodes. The Ba reinforcements, thermionic properties, and emission properties of the Ba- rare earth-O systems have also been observed. The exploration of the physical and chemical processes in these lamps requires more sensitive techniques due to the high temperature.

Barium has a considerable importance in lighting technology as a work function lowering element, which is shown in the Richardson-Dushman equation where a lower work function and a higher thermionic current are achieved at the same temperature. For that reason, the investigation and lowering of the work functions critical to these lamps.

After systematization of the referring literature, I have modeled the interaction between the emission material and tungsten surface by carrying out experiments on tungsten foils. The polycrystalline tungsten surface was covered with emission materials, such as Ba₂CaWO₆ and Ba₃Y₂WO₉, and then heated at a high temperature similar to the cathodes in the conventional industrial technology. The layer structure that evolves during sintering was investigated by XPS (X-ray Photoelectron Spectroscopy) and AES (Auger Electron Spectroscopy) methods. The work
function was monitored by WFS (Work Function Spectroscopy). By heating the samples in UHV conditions up to 700°C, it was possible to explore the temperature dependence of Ba. After comparing the physical and chemical properties of the two emission materials, the work function and elemental distribution of the cathode tips were discovered. The AES method, the WFS method, and Kelvin Probe were used as the function of sintering temperature and lamp operation time.

I made an attempt to achieve a lower work function by preparing a new emission material containing Sc and Y, exploiting the properties of Scandium. The emission materials with the chemical formula of \( \text{Ba}_2\text{Y}_x\text{Sc}_{2-x}\text{WO}_9 \) (0 \( \leq x \leq 2 \)) were synthesized by sintering mixtures such as \( \text{BaCO}_3 \) (as a source of BaO), \( \text{Y}_2\text{O}_3 \) or \( \text{Sc}_2\text{O}_3 \) and \( \text{WO}_3 \), in stoichiometric ratios, Ar atmosphere, and at 1450°C. The structures of the evolved materials were investigated by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) using both Energy Dispersive Spectroscopy (EDS) and Selected Area Electron Diffraction (SAED).

The studies also aimed to use the newly prepared emission materials in pilot HPS lamps and compare the most critical parameters (lamp voltage raise, initial lumen output, D-Line maintenance, Na loss/pressure drop) with those of the currently used commercial lamps.

The doctoral studies were performed in collaboration between Budapest University of Technology and Economics and General Electric Consumer & Industrial (Tungsram).

**SUMMARY OF SCIENTIFIC RESULTS**

**I. I revealed the interaction between the emission material and tungsten surface by carrying out experiments on tungsten foils**

I.1 I established and compared the temperature dependence of Ba diffusion at two emission materials, \( \text{Ba}_2\text{CaWO}_6 \) (BCT) and \( \text{Ba}_3\text{Y}_2\text{WO}_9 \) (BYT). In the BCT case, the Ba diffusion started at 450°C (Ba/W concentration ratio 0.0031), while at 600°C (Ba/W concentration ratio 0.0060) for the BYT case. I detected that BaO evolves on the W surface after high temperature heating at 1650°C. The other components of the emission materials, such as Ca and Y, were not detectable in this temperature range.

I.2 The following layer structure evolves on the W surface as the result of the reaction with Ba-containing emission materials at 1650°C in Ar atmosphere:

<table>
<thead>
<tr>
<th>Adsorbed O and C</th>
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<tbody>
<tr>
<td>Ba-O</td>
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<tr>
<td>Tungsten oxide and elemental W (( \text{BYT}<em>{\text{woc/wat}} &gt; \text{BCT}</em>{\text{woc/wat}} ))</td>
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<tr>
<td>Elemental W</td>
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</table>
Using XPS and WFS methods, the experience established that the W layer is more in the oxidized state than in case of BCT under the BaO layer. The Ba diffusion results confirm that statement, where the Ba diffusion started at higher temperature at BYT, leaving more time for oxidation of the tungsten foil.

The concentration results imply that the BaO coverage is less than a monolayer (60%) at each sample.

II. I revealed the composition and work function of HPS lamp cathode tip’s, as a function of sintering temperature and operation time

II.1 By WFS method it has been established that the cathode’s work function ($\Phi$) raises with its sintering temperature: the work function is lower on the tip of cathode sintered at 1500°C than the commercial used ones at 1650°C ($\Delta \Phi = 0.6$ eV). The reason of this effect could be the change of the bounding state of the oxygen: due to the higher sintering temperature the bonding of the oxygen to tungsten changed from physical to chemical resulting tungsten oxide and higher work function.

II.2 By AES method it has been established that the BaO-coverage is not homogenous, rather it forms islands on the cathode tips already at 100 h burning time. After 1000 h burning time the Ba is not detectable on the surface (below AES detection limit 1%).

III. Preparation and structure investigation of new Sc- and Y-containing emission materials

III.1 Similarly to the recipe of Ba$_3$Y$_2$WO$_9$, I prepared the Ba$_3$Sc$_2$WO$_9$ emission material by a new and shorter process, sintering mixtures of precursors such as BaCO$_3$ (as a source of BaO), Sc$_2$O$_3$ and WO$_3$, in stoichiometric ratios (3:1:1 respectively), in Ar atmosphere at 1450°C. The structure of the evolved material was investigated and by XRD.

III.2 The assumption made by XRD, namely Ba$_3$Y$_{0.6}$Sc$_{1.4}$WO$_9$, Ba$_3$YScWO$_9$ and Ba$_3$Y$_{1.4}$Sc$_{0.6}$WO$_9$ can not be described as homogeneous compound but an aggregation of phases with different compositions, has been confirmed by TEM method.

III.3 Based on the XRD patterns and Vegard law, the following evolved phases in the case of Ba$_3$Y$_{0.6}$Sc$_{1.4}$WO$_9$, Ba$_3$YScWO$_9$ and Ba$_3$Y$_{1.4}$Sc$_{0.6}$WO$_9$ were found after the sintering: Y-rich, Sc-rich and a mixed (Y, Sc) phase.

III.4 Based on the XRD patterns and TEM, it has been established that the structure of Ba$_3$(YSc)WO$_9$ is analogous to that of the Ba$_2$Y$_{0.667}$WO$_6$ structure and the chemical composition of the emission materials coincides with BaY$_{0.666}$W$_{0.334}$O$_3$. Since the duplication of the unit cell
of BaY_{0.666}W_{0.334}O_{3} gives the unit cell of Ba_{2}Y_{0.667}WO_{6}, a correlation between structure and composition can be established.

**SUMMARY**

Both the cathode and the emission material play a significant role in the HPS lamps. The surface analytical investigations at high temperatures had some technical difficulties, but we can contribute to understand the processes in these lamps under UHV conditions at room temperature.

In this thesis, I compared the physical and chemical properties (such as work function, layer structure, Ba diffusion) of emission materials that are currently used in industry, and I presented elemental distribution and work function results on cathode tips. I also investigated and used newly prepared emission materials in pilot lamps. The observed data was compared to the pilot lamps that had the BCT and BYT. It can be established that the new emission materials have at least as good parameters as the currently used ones.

The measurements were performed in the complex surface analytical system of the Budapest University of Technology and Economics Department of Atomic Physics, where XPS (X-ray Photoelectron Spectroscopy), AES (Auger Electron Spectroscopy), and WFS (Work Function Spectroscopy) methods are settled. The XRD (X-ray Diffractions) measurements were performed at Hungarian Academy of Sciences, Institute for Geochemical Research. The TEM measurements were carried out at Hungarian Academy of Sciences, Research Institute for Technical Physics and Material Science.

**DISSERTATION RELATED PUBLICATIONS AND CONFERENCES**


VIII. I. Beck, Electron emission properties of tungsten electrodes measured by work function spectroscopy, Ph.D. Conference, Budapest University of Technology and Economics, Budapest, Hungary, 26 November, 2003

IX. I. Beck, Gy. Vida, Electron emission properties of tungsten electrodes measured by work function spectroscopy, Spring conference for Hungarian PhD students, Sopron, Hungary, 19-22. May 2003