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Plasma and Electrode Processes, Degradation Phenomena in High Pressure Discharge Lamps

(Effects of Dose Constituents and Micro Level Impurities on Lamp Performance)

Ph.D. Thesis

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1 Introduction

The latest and most promising representatives of modern high intensity discharge (HID) light sources are metal halide lamps. These lamps were introduced in the early 60's of the 20th century. Their operating principles and construction details are in many respects very similar to that of high pressure mercury vapour discharge lamps, the classical members of the high intensity discharge lamp family. However, performance characteristics of metal halide light sources are significantly improved, thanks to the multiplicity of radiating plasma constituents with favourable ionisation, excitation and spectral properties contained in the chemical dose of the lamps.

The aim of my Ph.D. thesis is to discuss some questions and present some research and development results related to the design, electrode and plasma phenomena, and degradation processes caused by the extremely high operating temperature and pressure of metal halide light sources.

2 Objectives

The price for the improved electrical and optical properties of metal halide lamps is the complexity of physical and chemical processes due to the sophisticated chemical composition of the chemical dose in the lamps. Up to now, because of this complexity, it has been impossible to create general and „first principles" modelling tools that could support the design efforts of these light sources. Designing a metal halide lamp these days is still combining the predictions from partial theoretical computer models and the results from statistically established and evaluated practical experimental work.

The purpose of my work being presented in this Ph.D. thesis is to improve the design characteristics (that is the electrical and optical properties), and reliability of HID lamps, especially that of metal halide lamps. The foundation of these improvements are the design solutions that are developed via detailed analysis of some well-defined, relatively independent and self-consistent physical and chemical lamp phenomena.

My observations on a new electrode phenomenon of HID electrode operation, the experimental results on the formulation of an optimised metal halide dose composition, my proposed method to increase the positioning accuracy of electrodes in the arc chamber, and the computer modelled details of acoustic resonance phenomenon excited in the discharge vessel are related to the design development of metal halide lamps.

Lamps, like any other industrial products, are supposed to have acceptable useful product life and reliability. The gradual deterioration of performance through life is connected to the degradation processes taking place in the discharge vessel of the lamps. In my thesis I discuss our newly developed destructive and non-destructive methods to measure the gas composition and the impurity levels of different contaminants in the discharge plasma, and some explored details of chemical corrosion processes taking place either between the high temperature metal halide dose and the electrode assembly, or between the chemical dose and the discharge chamber wall.

3 Experimental

In order to follow the principles of operation of different lamp components (electrodes, current lead-throughs, quartz discharge vessel, etc.) or the time evolution of corrosion and degradation processes, up-to-date equipment of X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were intensively used, besides the widely used and conventional optical and electron microscopic (SEM) methods.

Both analytical methods are very surface sensitive. This is because the results of measurement are deduced from the kinetic energy distribution of released electrons, the mean free path of which is only a few atomic layers long in solid-state samples. In other words, the collected electrons having the proper energy for analysis can only be originated from depth of some atomic layers below the surface of the sample. Due to this surface sensitivity, the measurements have to be performed under ultra high vacuum conditions. Any contamination from the environment on the surface is also detected, and thus affects and may significantly modify the final measurement results. The sensitivity of the XPS method is in the order of one tens of atomic percent, while it is about one atomic percent in the case of AES. The difference between the two methods comes from the principle of primary excitation. The XPS method uses X-ray photons, while the sources of primary excitation are electrons at the AES method.

In addition to the application of these surface analytical methods, I have developed and supervised the construction work of an „in situ" high temperature mass spectroscopic test equipment for destructive gas composition measurement. It makes the determination of chemical composition and the contamination levels of impurities in the filling gas of metal halide lamp arc tubes possible under "close to real lamp" operating conditions. In this measurement the arc chamber of the lamp is fractured under ultra high vacuum conditions

while it is being operated at steady-state operation mode. Then the composition of the released hot gases is analysed by mass spectroscopic methodology.

In parallel with the development of this destructive measurement method, I also evaluated the feasibility of several non-destructive gas impurity testing principles. Out of these, in my thesis I concentrate on the non-destructive test method that is based on the measurement of the DC glow discharge voltage excited in the discharge vessel of the metal halide light sources to be analysed.

4 New results of research and development - Thesis

Results related to electrode operation phenomena 1-2

1

Based on Auger electron spectroscopic analysis, I concluded and confirmed that under ordinary processing temperature conditions (< 2300 K) of thoriated tungsten electrodes for high intensity discharge lamps the sole sources of the Th monolayer responsible for reducing the work function of the electrode surface are the submicron sized ThO_2 grains dispersed along the surface [1].

Under steady-state lamp operating conditions the thorium coverage on the surface of the electrodes is a result of a delicate balance between the dissociative and diffusion processes supplying thorium to the surface, and desorption and evaporation processes depleting thorium from it. With studies revealing the time and temperature dependence of thorium coverage on the surface of thoriated tungsten wires I demonstrated that at the operating temperatures of high intensity discharge lamp electrodes (typically 2500-2900 K) the depletion processes dominate. Consequently, formation of a stable thorium monolayer on the surface is not predictable, provided that only these processes are taken into account.

2

In connection with the Auger electron spectroscopic studies performed on thoriated tungsten electrode wires of high intensity discharge lamps, I identified a new phenomenon, namely the electron-induced dissociation of ThO_2 grains [2, 3], which has not been studied so far.

It was found, that besides the generally applied heat treatment at 1400-2300 K temperatures the exciting electron beam irradiation from the Auger analysis equipment itself was also required for the evolution of thorium coverage as a result of dissociation of ThO_2 grains on the surface. Under typical Auger electron spectroscopic measurement conditions (1.0-2.5 keV electron beam energy, 350 nm electron beam diameter) there a minimum threshold also exists for the current density of the exciting electron beam so as one to be able to detect any thorium coverage. This current density threshold is in the order of 10-100 $\mu A/mm^2$.

The phenomenon of electron-induced ThO_2 dissociation has also been confirmed by independent scanning electron microscopic (SEM) studies on the surface of thoriated tungsten electrode samples.

The conditions of an Auger electron spectroscopic analysis are significantly different from the conditions characteristic of the electron beam energies and current densities in real high intensity discharge lamps (1-10 eV electron beam energy, significantly higher current densities). However, it cannot completely be disregarded that the revealed electron induced dissociation phenomenon of ThO_2 yet may take place in the operation of lamp electrodes. This is especially true for the ignition phase of lamp operation, when the high accelerating voltage supplied by the ignitor circuit (2-25 kV) and the low gas pressure leads to electron kinetic energies approximating the exciting electron energies applied in Auger electron spectroscopic studies. During the very first ignition period of the lamps this electron-induced dissociation can be the only process that might create thorium coverage on the surface of the lamp electrodes and lower their work function.

Results related to the design of high intensity discharge lamps 3-5

3

I have developed a new metal halide chemical dose system [4], the main components of which are rare-earth metal halide compounds having wide-band radiation in the visible electromagnetic spectrum with (1) green and (2) red-blue/purple colour hue (e.g. cerium iodide plus dysprosium iodide), (3) alkaline halide(s) ensuring good electrical conductivity and arc stability of the discharge plasma with preferably intensive emission lines in the visible range (e.g. sodium iodide), and (4) a narrow-band emitter component (e.g. thallium iodide) of preferably low boiling point and high volatility.

By the help of the outlined combination of constituents of the newly developed metal halide dose system, I was able to achieve that the colour hue change of the lamps caused by a 10-15 % change of lamp input power was less by 50-80 %, compared to the colour hue change observable on lamps dosed with the most up-to-date metal halide dose systems known in the literature and used in lamps on the market today.

The colour hue of the lamps in this way becomes much less sensitive to the lamp power variations caused by the imperfections in the production process of the lamps, by the variations of the electric control circuit parameters, or by the disturbances in the electric network. In other words, the colour difference between lamp samples from the same population and under slightly different operating conditions becomes significantly lower. This is particularly important in indoor lighting applications that are more sensitive to colour consistency and colour quality [5, 6, 7, 8]. At high colour temperatures (4200 K, 5500 K) there has been no such metal halide dose system known for lamp designers.

An additional advantage of the newly developed metal halide dose system is its approximately 10-15 % gain in lamp efficacy.

4

By the help of extreme value analysis and Monte Carlo computer simulation method I evaluated the distribution of arc gap length, as a statistical variable, in double-ended quartz discharge chambers of high intensity discharge light sources. Based on the results of these analyses, I developed a new and easily applicable method for the alignment of the electrode assemblies [9] that can substantially reduce arc gap length variability (range and standard deviation).

In this new alignment method it is assumed that the lateral displacement of the electrode tips from the ideal line of arc tube axis is significantly different in the plane of the molybdenum sealing foil of the electrode assembly, and in the plane perpendicular to the plane of the foil. That is, the distribution of this lateral displacement is strongly non rotational symmetric. This is a valid assumption that is supported by experimental data, and is the result of the characteristics of lamp parts and lamp making process steps.

The plane of the molybdenum foils of the electrode assemblies at the two opposite ends of the discharge chambers is conventionally parallel to each other. In accordance with my new electrode assembly alignment method the plane of the two foils of the opposing electrode assemblies are to be aligned perpendicularly to each other. It is easy to realise that in this way the range (variability) of the statistical distribution describing the

deviation of arc gap from its nominal value is greatly reduced, just because of simple geometrical reasons. This improvement in arc gap variability is very cost-effective, since it does not require any additional expensive process development efforts (like increasing the geometrical accuracy of lamp components or processes).

The reduction in arc gap variability (range of population) does depend on the specific arc tube design geometry, and typically is in the order of 10-40 %. As a result of improved arc gap control, all of the main electrical and optical lamp performance characteristics are also improved, and the individual lamp samples become much more similar to each other.

5

Under my supervision, a finite element (FEM) computer modelling code has been developed that is capable to calculate the resonant eigenfrequencies, and the spatial velocity and pressure distribution of eigenmodes of acoustic resonance phenomenon excited in arc chambers of high intensity discharge lamps [10]. The computer code performs the solution of the wave equation with boundary conditions that neither require the homogeneity of temperature – and thus velocity of sound – spatial distribution across the volume of the discharge vessel, nor rotational symmetry of this temperature distribution. Under these conditions the calculation is also capable to handle the fact of “arc bowing”, that is the loss of rotational arc symmetry in horizontally operated arc tubes where convective gas flows cause the arc to be “bent” upwards.

By the help of our FEM code, spatial distribution of the eigenmodes and the values of resonance frequencies were determined for low wattage metal halide lamp (e.g. automotive gas discharge lamp) discharge chamber geometries. Based on the results of calculations, I could identify those frequency windows of operation in the 100-550 kHz frequency range that are free of arc instabilities caused by acoustic resonance effects. Such arc instabilities arise when the eigenmodes of the arc chamber are excited by the pulsed electric power drive on the lamps. The resonance free frequency windows define the permitted operating frequencies of a hypothetical high frequency electronic lamp drive and control unit, which may be produced with much lower production cost.

The spatial inhomogeneity of temperature distribution in the arc chamber reduces the width of allowable resonance free frequency windows due to breaking up the degenerated eigenfrequencies of the cavity. Our computer model can approximate the real pressure and gas velocity distributions much better than any other published

computer code so far. In this way, electronic designers can have more accurate predictions about the required frequency stability of the high frequency electronic control unit under development.

Results related to corrosion and degradation phenomena 6-9

6

An “in situ” high temperature lamp analysis tool have been developed and built in which impurities in the discharge chamber and the gas composition of discharge plasma of high intensity discharge lamps can be analysed under circumstances approximating the real conditions of operating lamps [11, 12]. The principle of operation is as follows. The intact arc tube of the high intensity discharge lamp to be analysed is switched on inside a vacuum chamber. When the arc tube has reached its steady state operating conditions, it is fractured. The released hot gases are transferred by a metal capillary into an analysis chamber of a quadrupole mass spectrometer as fast as it is possible, that is much faster than the equilibration time of the hot gases with the cold vacuum chamber walls.

With the help of this equipment it becomes possible to compare mass spectroscopic results obtained under “close to real lamp operating conditions” to the impurity values measured in arc chambers fractured at room temperature by the conventional method. In this way, one can establish a correlation between the two methods, and “calibrate” the easier and faster room temperature measurements.

Based on the measurement results, I was able to identify the most critical contaminants of metal halide lamp arc tubes (water, hydrogen, carbon monoxide, nitrogen, argon), locate their sources, and analyse the efficiency of the actions for improvements in the lamp making process.

The most important source of water contamination turned out to be the metal halide dose, which is highly hygroscopic and can take up several thousand ppm of water if handled improperly. Metal halide doses can safely be processed in high purity argon dry-box systems. The water impurity level can further be reduced by processing time reduction and with application of high temperature dosing equipment. Water dissociates into hydrogen and oxygen. The former causes ignition and arc instability problems, the latter reduces the “effective” amount of metal halide dose by oxidising a part of it. Carbon monoxide primarily comes from graphite-base drawing agents of electrode assembly components, and from reduction of carbon dioxide adsorbed from air on surfaces.

Electrode assembly cleaning significantly reduced the level of carbon monoxide. The source of nitrogen contamination is primarily also the adsorption from air, or leaks of the pump and dry-box system. Argon is a residual gas from the dry-box system. If its level is below some percent, it has no significant effect on discharge operation. The level of argon impurity was reduced by increasing the number of arc tube pumping cycles. However, this is limited by processing time and machine speed constraints.

7

I worked out several non destructive methods to detect and measure the impurity levels of the most important gas contaminant of high intensity discharge plasmas, namely hydrogen. Out of these methods, the measurement of “glow discharge voltage” turned out to be the most suitable one for analytical purposes. In this method, the lamp is operated at low DC current driving conditions and enforced into “glow discharge mode”. I concluded that the value of the DC glow discharge voltage measured on lamp terminals is strictly monotonically related to the level of hydrogen contamination of the discharge gas.

I proved that the sensitivity of this non destructive method is high enough to make the quantitative measurement of hydrogen contamination levels possible in the range when hydrogen has considerable - but still not catastrophic - effect on lamp operation. The accuracy of the measurement at low hydrogen concentrations (< 500 ppm) and low glow mode currents (< 0.5 mA) is in the order of 100 ppm, presuming that the required time constraints for lamp stabilisation are strictly taken into account.

8

By the help of X-ray photoelectron spectroscopic (XPS) and atomic absorption spectroscopic (AAS) analysis, I followed up the time evolution of degradation processes taking place between the metal halide dose and the molybdenum current conducting foil in the glass-to-metal seals of metal halide lamps.

Our model studies, in parallel with experiments conducted on real lamps, confirmed that sodium iodide is one of the most corrosive materials in the metal halide dose from the molybdenum corrosion in the glass-to-metal bond perspective [13, 14, 15]. Formation of porous structured sodium molybdate (Na_2MoO_4), as a result of high temperature chemical reaction between sodium iodide and molybdenum, leads to destruction of Mo-MoO_2-SiO_2 chemical bond [16] between the molybdenum foil and the quartz arc

tube material in the originally vacuum-tight glass-to-metal seal, and finally causes lamp failure.

On the other hand, other metal halide dose components like indium iodide do not cause serious degradation in the glass-to-metal seal, since chemical reaction of molybdenum with these chemicals does not take place. Indium-iodide is simply diffusing into the deeper layers of the molybdenum foil as time goes on.

These measurement results are in line with the life test results obtained on real lamp samples having different metal halide dose compositions.

9

Based on X-ray photoelectron spectroscopic (XPS) analysis, it was possible to follow the time evolution of diffusion and implantation of metal halide dose and electrode constituents, as well as discharge gas contaminants into the quartz discharge chamber wall. I found that the amount of dose components (Na), and also that of the evaporated and sputtered materials from the electrodes (W, Th) in the discharge vessel wall is monotonically increasing in time. In addition, due to the small ionic radius of sodium, this element is continuously diffusing out of the arc chamber volume and lost from the discharge plasma, which has been confirmed by secondary-ion mass spectroscopic (SIMS) measurements on the outer surface of the arc tubes.

Our additional XPS measurements revealed that SiC is also formed in the quartz arc tube wall in time. The SiC formation is supposed to be the results of CO contamination of the discharge gas and the extremely high operating temperature of the wall. Such chemical reaction is known from other area of technology, where SiC is being created on SiO_2 surface by high temperature heat treatment of the SiO_2 wafer in CO atmosphere. This fact supports our assumption on the role of CO contamination of the discharge plasma in this degradation reaction of the quartz discharge vessel wall.

As a result of these reactions, the fused silica arc tube material is being re-crystallised (transformed into the thermodynamically more stabile crystalline phase), and its optical transparency and mechanical strength is gradually being reduced.

5. List of publications directly related to Ph.D. Thesis:

1. Á. Böröczki - I. Gaál - S. Gurbán - M. Menyhárd - L. Petrás - L. Balázs:
   Dissociation of thorium oxide on the surface of free surface tungsten
   (10th International Symposium on the Science and Technology of Light Sources, Toulouse, France, Poster No. 203, 2004, Proceedings, IOP Publishing Ltd.)
2. Á. Böröczki - I. Gaál - S. Gurbán - M. Menyhárd - E. Horváth - A. L. Tóth - L. Petrás - L. Balázs:
   Electron stimulated thorium adatom enrichment on the surface of thoriated tungsten below 2300K
   (*16th International Plansee Seminar, Reutte, Austria, Paper No. 304, 2005, Proceedings, Plansee Holding AG*)
3. Á. Böröczki - I. Gaál - S. Gurbán - M. Menyhárd - E. Horváth - A. L. Tóth - L. Petrás - L. Balázs:
   Electron stimulated thorium adatom enrichment on the surface of thoriated tungsten below 2300K
   (*International Journal of Refractory Metals and Hard Materials, Volume 24, Issue 4, July 2006, pp. 343-349, Elsevier Ltd.*)
4. Boroczki, Agoston:
   High pressure mercury vapour discharge lamp with reduced sensitivity to variations in operating parameters
   (*European Patent Applications, EP 1 134 776 A2, 15.11.2000*)
5. Scott, Curtis Edward – Boroczki, Agoston – Tambiny, Anthony John – Greskovitch, Charles David – Preston, Barry:
   Single ended ceramic arc discharge lamp and method of making the same
   (*European Patent Application, EP 1 111 654 A1, 20.12.2000*)
6. Ágoston Böröczki – István Csányi – Sándor Holló – Michael R. Armbruster:
   Lighting system for well-defined beam pattern generation using ceramic metal halide lamp as the light source
   (*United States Patent, US 6,536,918 B1, Aug. 23, 2000*)
   (*World Intellectual Property Organization, WO 02/17350 A1, 28 February, 2002*)

7. Ágoston Böröczki:
   Development of a Discharge Automotive Lamp and its Launch of Production
   (*National Research and Development Programs, 3rd Program, „Advanced Methods and technologies" conference, Bureau for National Research and Technology, 2004*)
8. Ágoston Böröczki:
   Development of a Discharge Automotive Lamp and its Launch of Production
   (National Research and Development Programs, 3rd Program, project leader of project No. OM 3 045/2001, periodic technical reports (10) and summary reports (2), 2001-2004.)
   (lecture on the conference presenting the eight most successful NRDP projects, Presentation Room in the Hungarian Academy of Sciences, May 19, 2003)
9. M. Gyukics – P. Maák – L. Jakab – P. Richter – T. Torma - Á. Böröczki:
   A computational model for simulating volume-emitters in arc lamps
   (10th International Symposium on the Science and Technology of Light Sources, Toulouse, France, Poster No. 152, 2004, Proceedings, IOP Publishing Ltd.)
10. Boroczki, Agoston:
    Electrode arrangement for a discharge arc chamber
    (*European Patent Application, EP 1 197 984 A1, 11.10.2001*)
11. Attila Vágvölgyi - Ágoston Böröczki – Szabolcs Gyimóthy – Imre Sebestyén:
    Modeling acoustic resonance in high-pressure discharge lamp arc chambers
    (International Journal of Applied Electromagnetics and Mechanics No.13 (2001/2002) pp. 427 - 430, IOS Press)
12. Ágoston Böröczki - Péter Kovács - György Hárs:
    Investigation of gas composition on discharge lamps fractured during operation by means of mass spectrometry
    (*Measurement Science and Technology, 16 (2005) 1–5, IOP Publishing Ltd.*)
13. Péter Kovács – Ágoston Böröczki – György Hárs:
    Investigation of Impurities in High Intensity Discharge Lamps by Destructive Methods with Quadrupole MS
    (*JVC11, Joint Vacuum Conference, Prague, Czech Republic, Poster No. PW35, 2006*)
14. Á. Böröczki - G. Dobos - K. Josepovits – Gy. Hárs:
    Surface Analytical Studies on Corrosion Reactions of Metal Halide Salts
    (EMAS 2005 / IUMAS-3, European Microprobe Analysis Society, Florence, Italy, Conference Poster, 2005)

15. Á. Böröczki - G. Dobos - K. Josepovits - Gy. Hárs:
    High Temperature Reactions between Molybdenum and Metal Halides
    (*Applied Surface Science 252 (2006) 8309-8313, Elsevier Ltd.)*
16. G. Dobos - Á. Böröczki - K. Josepovits:
    High temperature reactions between molybdenum and metal halides
    (*COST Materials Action 529, „Efficient Lighting for the 21st Century", 2nd Work Group Meeting on Materials Issue in Lighting Technology, Budapest, Paper, 2006*)
17. Gábor Dobos – Katalin V. Josepovits – Ágoston Böröczki – István Csányi –
    György Hárs:
    Heat Treatment of Molybdenum under Vacuum Conditions
    (*JVC11, Joint Vacuum Conference, Prague, Czech Republic, Poster No. PM1, 2006*)