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Thermodynamic investigations of corrosion phenomena caused by metal halide salt melts in high temperature discharge lamps

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Discharge vessels of advanced light sources are made of translucent polycrystalline Al_2O_3 (PCA). These tubes contain salt mixtures, which essentially consist of metal halides. The salt mixture is present as a melt at the coldest spot of the vessel under operating conditions and vaporizes partly. The temperatures of the coldest spot range between 1200 K and 1300 K, depending on the lamp performance. The maximum wall temperatures range up to 1500 K and for special purposes up to 1700 K. Important constituents of the melt are alkali halides AX (A = Na, Cs, X= Br, I) and rare earth metal halides LnX_3 (Ln = Dy, Ho, Tm). Severe corrosion attack on the wall material is observed in the PCA discharge vessels. The aim of this work is to elucidate the corrosion mechanism.

Annealing experiments under well defined temperatures were carried out in order to understand the complex chemical corrosion processes. Two different annealing vessels were used, one for experiments under isothermal conditions with a temperature of 1473 K and one for experiments with a linear temperature gradient from 1450 K to 1600 K. The vessels were filled with salt mixtures of different compositions and annealed for 1000 h. The corrosion attack was characterised by XRD, analytical electron microscopy, high temperature mass spectrometry, and chemical analysis of the salt melts.

The results of our investigations show that the corrosion attack is caused by vapour species and by the salt melt. The most severe corrosion is observed in vessels filled with mixtures of alkali halides and rare earth metal halides. No corrosion of the alumina is practically observed if pure alkali halides or pure rare earth metal halides are present in the annealing vessel.

Keywords: thermodynamic, corrosion, lamps, metal halide salt

Introduction

Discharge vessels of advanced light sources are made of translucent polycrystalline Al_2O_3 (PCA) (Figure 1). These tubes contain salt mixtures that essentially consist of metal halides. The salt mixture is present as a melt at the coldest spot of the vessel under operating conditions and vaporizes partly. The temperatures of the coldest spot range between 1200 K and 1300 K, depending on the lamp performance. The maximum wall temperatures range up to 1500 K and for special purposes up to 1700 K. Important constituents of the melt are alkali halides *AX (*A = Na, Cs, X = Br, I) and rare earth metal halides LnX_3 (Ln = Dy, Ho, Tm*)*.

The vapour of the meatal halides enter the arc column and are used for the light emission.

During the lifetime of metal halide lamps progressive corrosion can be observed. Tungsten can be deposited on the cold parts of the burner. With the known tungsten cycle[1] this effect can be reduced. Severe corrosion attack on the wall material is observed in the PCA discharge vessels. Figure 2 shows a a cross section of a 35 W burner that has been operated for about 9000 h. As a dotted line the original shape of the discharge vessel is shown. It can be seen that in the near of the electrodes and in the hotter regions, where the molten salt is present during the operation, alumina is dissolved and transported away whereas it is deposite in the edges of the vessel. The aim of this work is to elucidate the corrosion and transport mechanisms of the alumina wall material and their influence on the gas phase chemistry. Studies on the high temperature lamp chemistry are reported by Hilpert and Niemann[2]. The results of investigations of the corrosion attack of discharge vessels made of quartz glass and PCA can be found in[3] and[4].

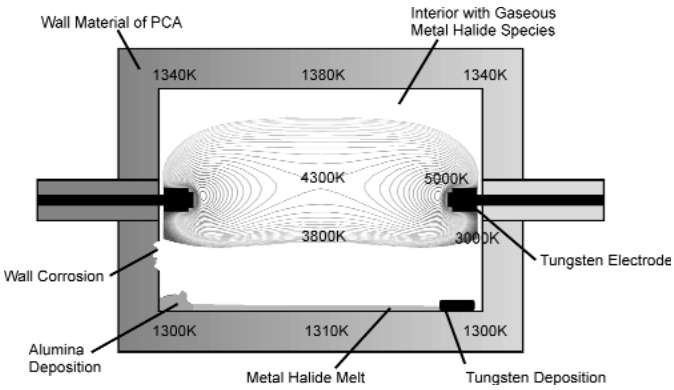

Figure 1 Schematic drawing of an arc tube of a metal halide lamp with temperature distribution under operating conditions

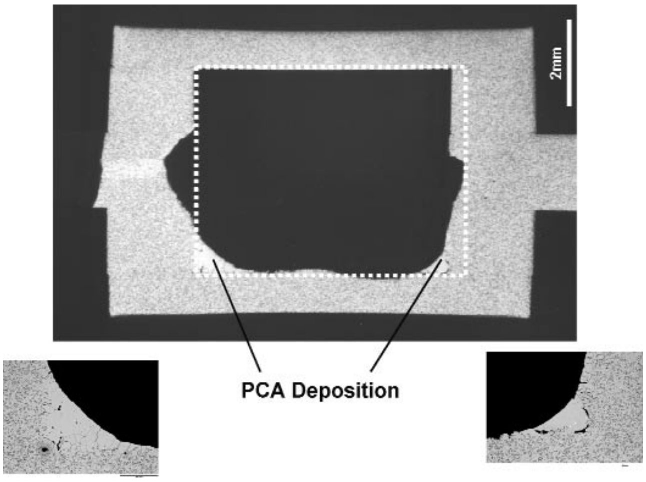

Figure 2 Cross section of a corroded discharge vessel in horizontal burning position (after 9000 h of operation)

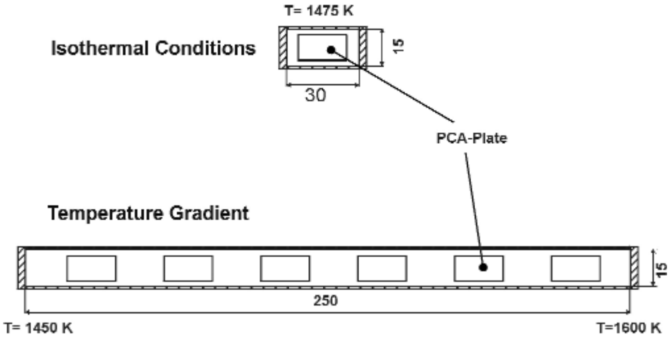

Figure 4 PCA vessels for annealing experiments under isothermal conditions and with temperature gradient

Experimental

Vaporization studies using Knudsen effusion mass spectrometry (KEMS), as well as annealing experiments with sealed alumina ampouls containing different salt mixture fills, were carried out in order to get a detailed insight into the chemical interactions between the wall material consisting of alumina at the inner surface and the salt mixture.

The Knudsen effusion mass spectrometer (see Figure 3) is a single focussing 90° sector field instrument of the type CH5 supplied by Finnigan MAT, Bremen, Germany[5]. The vapour species which effudate out of a one compartment Knudsen cell made of PCA in the terms of this work were ionized with an electron emission current of 82 µA and an electron energy of 15–21 eV. This experimental setup was used in order to simulate the conditions in the discharge vessel of a PCA lamp.

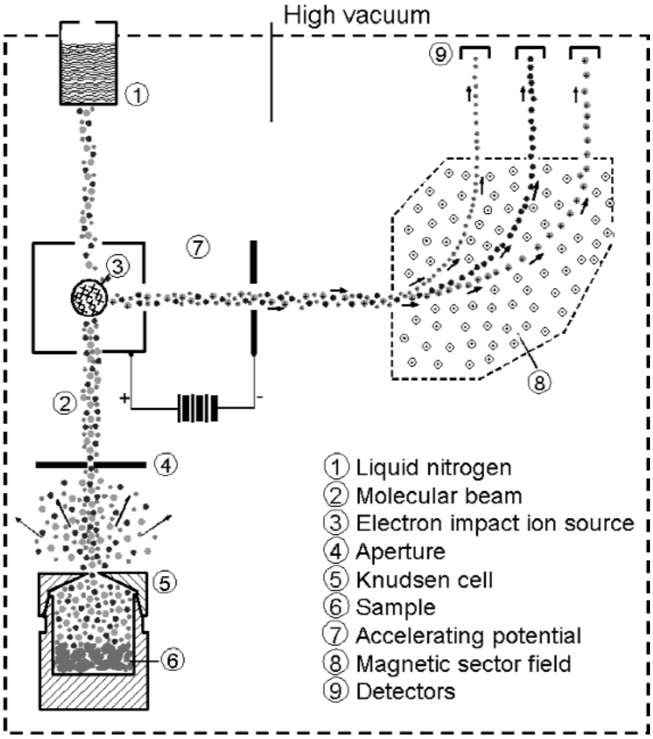

Figure 3 Schematic representation of the Knudsen cell mass spectrometer system

Mixtures of the systems NaX(l, g)/ TmX^3(l, g)/ Al_2O_3(s) with X = I, Br were analysed mass spectrometrically. Ion intensities of each vaporizing species were measured and partial pressures were computed by the use of Equation 1.

$$p(i) = k\frac{\sum_j I_j T}{\sigma_i} \qquad [1]$$

p(i)	partial pressure of gas species i
ΣI_j	intensity of ion species j
T	temperature
σ_i	ionization cross-section
k	pressure calibration constant

The pressure calibration was done with pure NaX *(*X = Br, I). From the resulting equilibrium constants of the examined corrosion reactions in these systems, the second and third law enthalpies of reactions were determined.

To carry out the annealing experiments, different PCA vessels were made for furnace experiments under isothermal conditions and in a temperature gradient (see

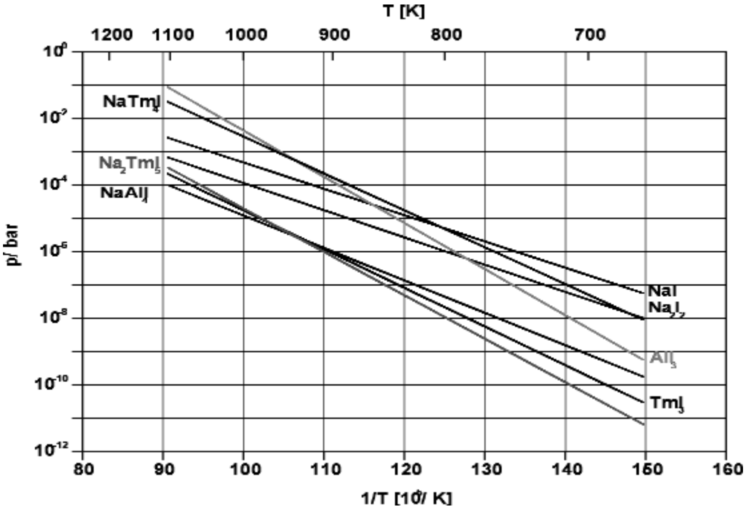

Figure 5 Partial pressures over an equimolar NaI/ TmI_3 /Al_2O_3 mixture

Table I
Ion species in the vapour of $NaX/ TmX_3/ Al_2O_3$ (X = Br, I) mixtures

Reactands in Knudsen Cell	
$TmBr_3(s)+NaBr(s)+Al_2O_3(s)$	$TmI_3(s)+NaI(s)+Al_2O_3(s)$
T-Range	
744–1134 K	842–1103 K
Identified Ions in Mass Spectrum	
Na^+, $NaBr^+$, Na_2Br^+, $AlBr^+$, $AlBr_2^+$, $AlBr_3^+$, $TmBr^+$, $TmBr_2^+$, $TmBr_3^+$, ($Tm_2Br_5^+$) $NaAlBr_3^+$, ($NaAlBr_4^+$) $NaTmBr_2^+$, $NaTmBr_3^+$, $NaTmBr_4^+$, $Na_2TmBr_4^+$	Na^+, NaI^+, Na_2I^+, AlI^+, AlI_2^+, AlI_3^+, TmI^+, TmI_2^+, TmI_3^+, $NaAlI_3^+$, $NaTmI_2^+$, $NaTmI_3^+$, $NaTmI_4^+$, $Na_2TmI_4^+$

Figure 4). The temperature for the isothermal experiments was choosen at 1475 K. The condition for the gradient annealing was a linear temperature gradient within 250 mm length. The cold end temperature was 1450 K, whereas the hot end temperature was 1600 K. The annealing time for both kinds of experiments has been 1000 h.

The fills of the PCA vessels were different compositions of the system $NaI-DyI_3$.

After the end of the experiments, the condensed salt melt was examined with chemical analysis. The corrosion phases of the PCA container material after the annealing experiments, as well as after the KEMS experiments, was studied by X-ray diffraction, XRD, and scanning electron microscopy, SEM.

Results and discussion

For the vaporization experiments, powder mixtures of NaX and TmX_3 (X = Br, I) were heated in a Knudsen cell made of PCA. The identified gas species in the mass spectrum and the temperature ranges of the measurements are given in Table I. TmX_3 was selected as lanthanide halide as an example. The vapor species X, $AlX_3(g)$, $NaX(g)$, $Na_2X_2(g)$, TmX_3, $Tm_2X_6(g)$, $NaAlX_4(g)$, $NaTmX_4(g)$, and $Na_2TmX_5(g)$ were identified in the equilibrium vapour and the partial pressures of the abundant species determined (Figure 5).

The vapour species $AlX_3(g)$ was detected in the vapour by mass spectrometry measurements over mixtures of $TmX_3/ NaX/ Al_2O_3$ and not over an NaX/ Al_2O_3 mixture. This indicates the corrosion attack of the PCA wall material by TmX_3. XRD analysis of annealed TmX_3/ Al_2O_3 powder mixtures showed the formation of a new amorpheous phase indicating the dissolution of Tm in Al_2O_3. In addition the phase $TmOX(s)$ was formed in the case of X=Br. The light technical relevance of the detected heterocomplexes are discussed in[6].

The results of the annealing experiments in PCA ampoules under isothermal conditions are shown in Figures 6 and 7 and for the investigation under a temperature gradient in Figure 8. The ampoules contained mixtures of NaI and DyI_3. The formation of the mixed oxides $Dy_3Al_5O_{12}(s)$ and $DyA_1O_3(s)$ as corrosion product were observed at the cold part of the PCA vessel after annealing in a temperature gradient over 1000 h. The annealing experiments show gas phase transport of Al_2O_3 from the hot part of the vessel to the cold part.

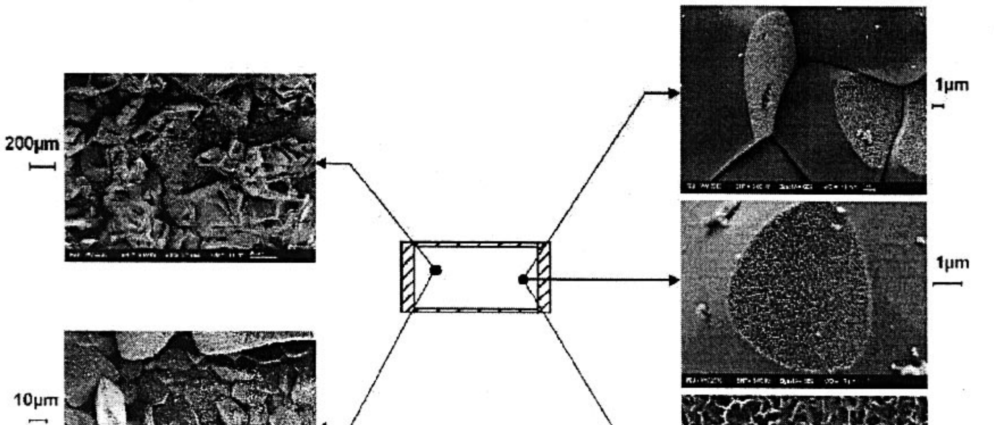

Figure 6 SEM investigation of a PCA vessel after isothermal annealing at 1473 K (5 wt% NaI)

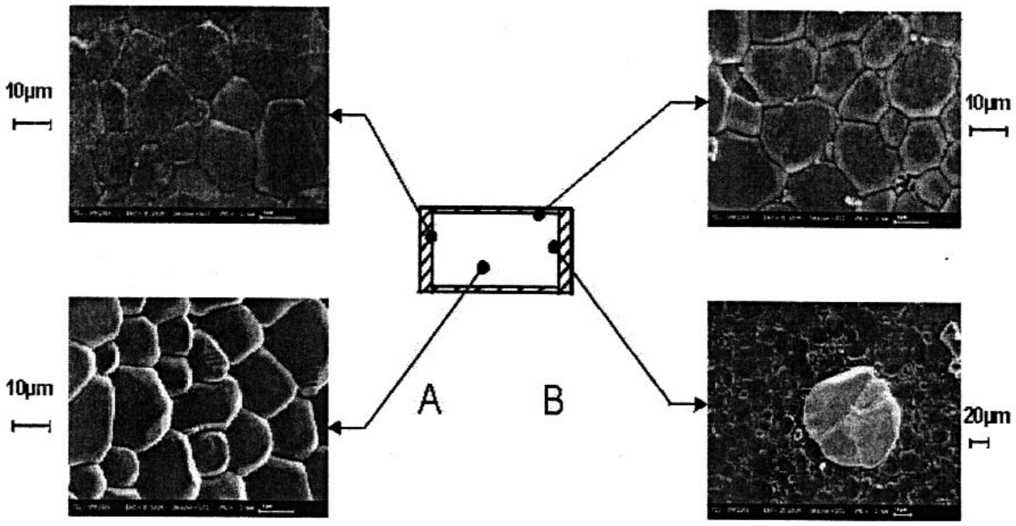

Figure 7 SEM investigation of a PCA vessel after isothermal annealing at 1473 K (90 wt% NaI)

During the isothermal experiments there was a small temperature gradient in the vessel because this vessel was annealed in a tubular furnace under flowing argon in order to avoid diffusion of oxygen through the PCA wall into the vessel. The argon flow caused a temperature gradient. The cold part of the vessel from the isothermal and gradient experiments showed the deposition of Al_2O_3 from the gas phase.

The corrosion attack of the cold part visible in the isothermal experiment differs from that in the gradient experiment. The former shows corrosion attack of the grains by which Al_2O_3 is exsolved from the grains into the gas phase, the latter the $Dy_xAl_yO_z$ formation as mentioned above. The gaseous species for the Al_2O_3 transport via the gas phase could be AlO(g) and AlOX(g). The species AlO*(g)* and AlOBr(g) were detected on leaking gaseous iodine and bromine into a Knudsen cell made of PCA and filled with PCA lumps at cell temperatures of up to 2000 K. A Knudsen cell with a gas inlet system was used for these studies. The discriptions of the gas phase transport equations of Al_2O_3 can be found in[7].

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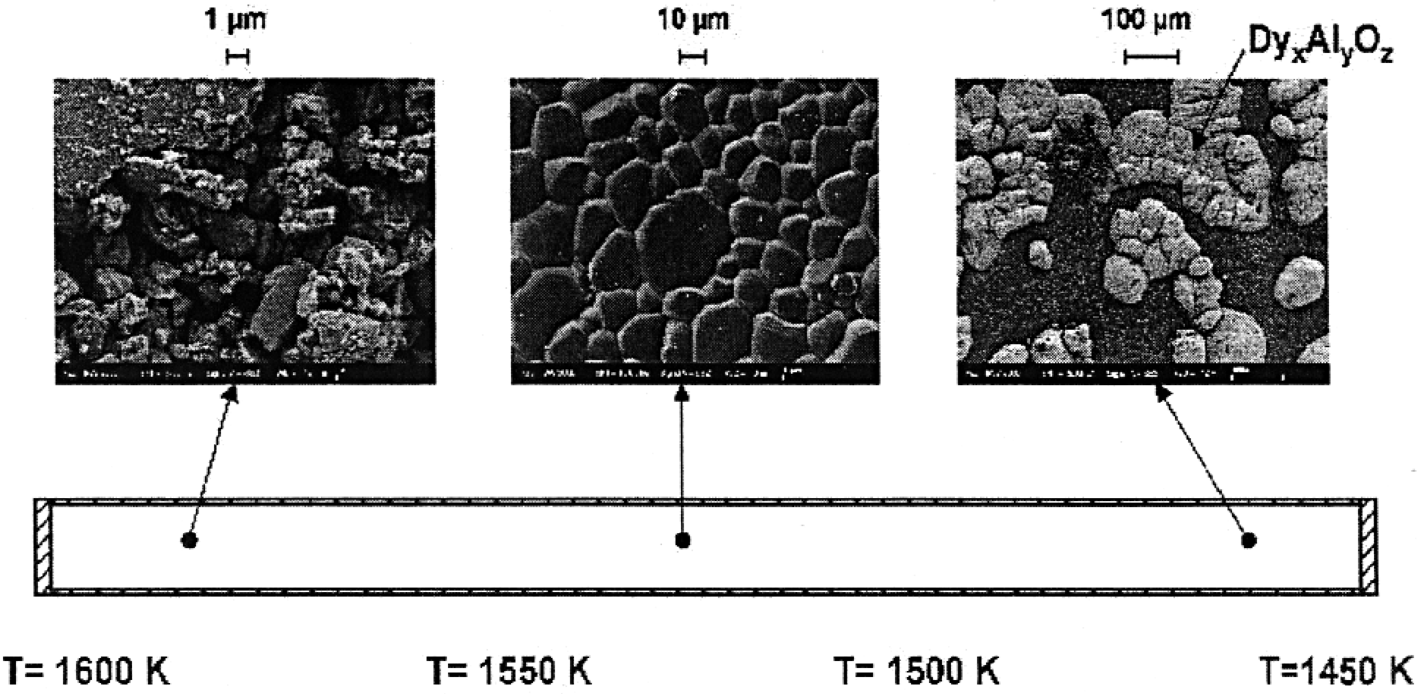

Figure 8 SEM investigation of the PCA vessel after the annealing in a temperature gradient (25 wt% NaI)

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