

HIGH TEMPERATURE CORROSION OF ALUMINA IN METAL HALIDE LAMPS

T. Markus, and K. Hilpert

Research Centre Jülich, Germany
IWV-2, D-52425 Jülich, Germany
T.Markus@fz-juelich.de

Introduction

Metal halide lamps have achieved a widespread acceptance due to their high luminous efficiency and good colour quality. At the beginning of their development these lamps were used for outdoor lighting e.g. the lighting of sportsfields. Since several years metal halide lamps are also used for indoor lighting and for the head lights of automobiles. The size of the discharge vessel of the lamps had to be reduced substantially by this development. The influence of high temperature lamp chemistry becomes the more important the smaller the discharge vessel is. These discharge vessels for advanced energy saving light sources are made of polycrystalline alumina (PCA). The lamps contain a salt melt which in part vaporize under operating conditions. Important constituents of the melt are for example DyI_3 , HoI_3 , TmI_3 , and NaI . Severe corrosion attack on the alumina wall material can be observed in the PCA discharge vessels (see figure.1).

Results

The vapor of the systems $\text{NaX} - \text{TmX}_3 + \text{Al}_2\text{O}_3$ ($\text{X} = \text{Br}, \text{I}$) was investigated under equilibrium conditions in the temperature range from 744 to 1134 K by using Knudsen Effusion Mass Spectrometry with a one compartment Knudsen cell and the partial pressures of the abundant species were determined. The identified gas species are listed in Table 1. AlX_3 vapor species result from corrosion reactions between the salt melt and Al_2O_3 . Figure 2 shows the partial pressures of the vaporizing species over an equimolar $\text{NaI} / \text{TmI}_3 / \text{Al}_2\text{O}_3$ mixture.

The determination of reliable values for the thermodynamics of corrosion reactions between the salt mixture and solid alumina is the aim of the mass spectrometric measurements. The formation of hetero complexes between salt components and additionally between NaX and AlX_3 (the latter arising from reaction between TmX_3 and alumina) could be observed and the enthalpies and entropies of formation of the hetero complexes were determined. Thermodynamic data (K_p , ΔH , ΔS) describing the stability of the complexes $\text{NaAlX}_4(\text{g})$, $\text{NaTmX}_4(\text{g})$ and $\text{Na}_2\text{TmX}_5(\text{g})$ were determined from the measured partial pressures.

To get a detailed insight into the chemical interactions between the wall material consisting of alumina at the inner surface and the salt mixture, annealing experiments with sealed alumina ampouls containing different salt mixture fills were carried out under isothermal conditions and in a temperature gradient in addition to the mass spectrometric measurements. The formation of the mixed oxides $\text{Dy}_3\text{Al}_5\text{O}_{12}(\text{s})$ and $\text{DyAlO}_3(\text{s})$ as corrosion products were observed at the cold part of the PCA vessel after annealing in a temperature gradient over 1000h (see figure 3). The annealing experiments show that Al_2O_3 is transported from the hot part of the vessel to the cold part. In addition to the experimental work, model calculations were carried out, which show, that the observed phenomena can be calculated by using the thermochemical data determined in this work.

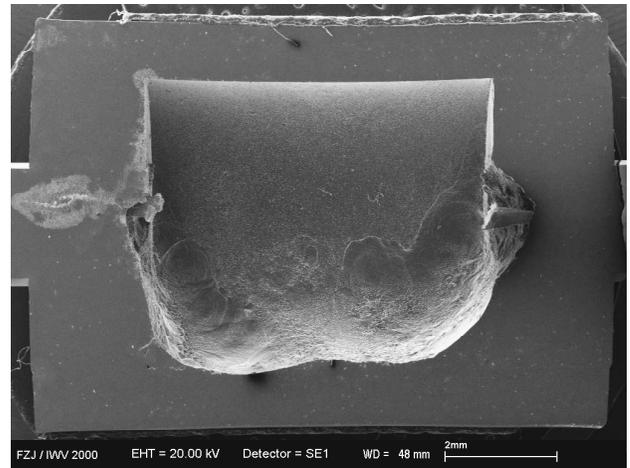


Fig. 1: Cross section of a PCA-discharge burner after 9000h of operation

Reactands in Knudsen Cell	
$\text{TmBr}_3(\text{s}) + \text{NaBr}(\text{s}) + \text{Al}_2\text{O}_3(\text{s})$	$\text{TmI}_3(\text{s}) + \text{NaI}(\text{s}) + \text{Al}_2\text{O}_3(\text{s})$
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^+ , $(\text{Tm}_2\text{Br}_5^+) \text{NaAlBr}_3^+$, (NaAlBr_4^+) NaTmBr_2^+ , NaTmBr_3^+ , NaTmBr_4^+ , $\text{Na}_2\text{TmBr}_4^+$	Na^+ , NaI^+ , Na_2I^+ , AlI^+ , AlI_2^+ , AlI_3^+ , TmI^+ , TmI_2^+ , TmI_3^+ , NaAlI_3^+ , NaTmI_2^+ , NaTmI_3^+ , NaTmI_4^+ , $\text{Na}_2\text{TmI}_4^+$

Table 1: Ion Species in the vapor of $\text{NaX} / \text{TmX}_3 / \text{Al}_2\text{O}_3$ ($\text{X} = \text{Br}, \text{I}$) mixtures

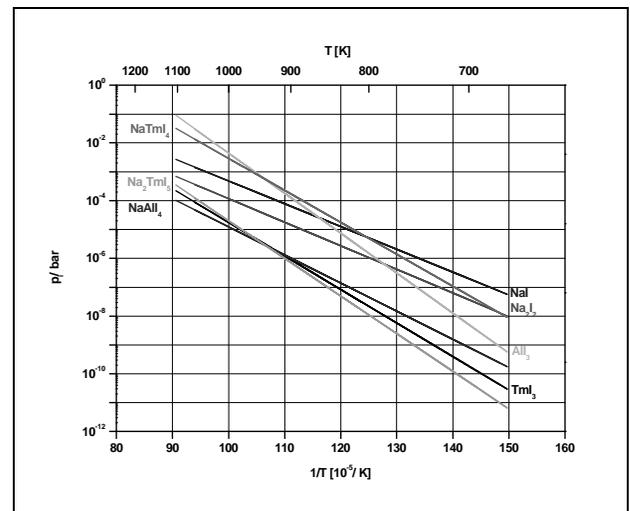


Fig. 2: Partial pressure over an equimolar mixture of $\text{NaI} / \text{TmI}_3 / \text{Al}_2\text{O}_3$

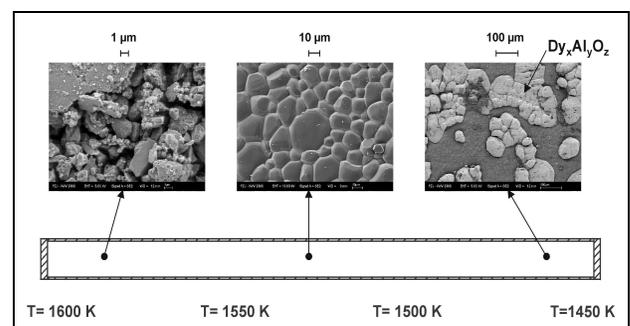


Fig. 3: SEM investigation of the PCA vessel after the annealing in a temperature gradient for 1000h