Carbon doping - A key for the substitute of thoriated tungsten

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Abstract

Thoriated tungsten is the state-of-the-art cathode material for short arc lamps used in cinema lighting and semiconductor lithography. The major effect of thorium is the temperature reduction at the cathode tip due to a lowered electron work function. The radioactive nature of thorium is driving the development of a substitute. Rare-earth-doped tungsten qualities have potential but lead to fluctuating light output, the so called flickering.

It is demonstrated that the flickering of lanthanated tungsten cathodes doped with carbon is comparable to thoriated tungsten. Two beneficial effects of carbon are found. High-temperature diffusion couples prove that carbon activates the diffusion of lanthanum. Thus flickering due to depletion of lanthanum at the cathode tip is prevented. Additionally, highly instrumented lamp tests prove the prevention of lanthanum containing deposits close to the cathode tip. Such deposits trigger the flickering since their low work function attracts the spot of the arc. Tests with commercial lamps confirm a stable light output by carbon doping but show increased blackening of the lamp bulb.

Keywords

Short arc discharge lamp, cathode material, substitute of thoria

Introduction

The operation condition of modern short arc lamps (SAL) imposes stringent requirements on the cathode material. The most extreme is the tip temperature close to the melting temperature of tungsten (3693 K). To maximize the electron emission of the cathode, the so-called emitter effect is exploited [1]. This effect is obtained by doping tungsten with elements which are electropositve compared to tungsten. During operation a monolayer of the emitter substance covers the cathode at the spot of the arc. The monolayer has a dynamic nature as it is understood as the balance of continuous evaporation and redeposition of the emitter substance from the plasma [2]. The monolayer constitutes an electric dipole layer on the

tungsten tip, by which the barrier for electron emission is lowered. The need of high thermal stability and electropositive behavior with regard to tungsten reduces the options for emitter substances to rare earth oxides, hafnia, zirconia and thoria. During decades of application, doping with thoria has become state of the art. Due to its radioactive nature many efforts have been undertaken to substitute thoria [3–7]. Many of these concepts are based on the use of rare earth oxides, e.g. the material WLZ (W + 2.5 wt.% La_2O_3 + 700 µg/g ZrO_2). Doping with these substances leads to a reduction of the electron work function comparable to thoriated tungsten. The main drawback of the thoria-free solutions is the less stable burning behaviour, the so called flickering. The addition of carbon in the bulk or in form of a carburized layer is described improving the stability of the light output [8–11]. Carbon is supposed to act as a reducing agent decomposing the emitter oxide. In principle the decomposition reaction can be described according to equation (1), see e.g. [9].

$$La_2O_3 + 3\,C \leftrightarrows 2\,La + 3\,CO \qquad (1)$$

The current work investigates the effect of carbon in depth. The influence on the diffusion behaviour of La in the bulk is studied by experiments with differently doped diffusion couples. Additionally, highly instrumented lamp tests in the “Bochum Model Lamp” give an insight into the effect of carbon during application. Finally, lamp tests with an industrial lamp type compare the burning behaviour of carbon doped Th free cathode material to thoriated cathode material.

Experimental

Material Description

The carbon-doped cathode material used for the present investigation consists of a tungsten matrix with 2 wt.% La_2O_3. The amount of the nominal carbon doping is 600 µg/g leading to the abbreviation WL20C600 for that material. For some samples the carbon content varies and is therefore indicated individually. An insight to the microstructure of the material is provided by a light optical micrograph (LOM) of a metallographic section, see Fig. 1. The grain boundaries of the tungsten matrix and the lanthanum oxide particles (black dots) can be recognized. During sintering the phase W_2C is formed which cannot be recognized by LOM but in phase maps obtained from electron back scatter diffraction (EBSD), an analytical method that is applied in a scanning electron microscope (SEM), see Fig. 2. It must be noted that most of the lanthanum oxide particles were removed by the special electrolytical preparation of the metallographic section required for EBSD. The presence of the phase W_2C is also confirmed by X ray diffraction (XRD) measurements.

The area fraction of the phase W_2C was determined by means of digital image analysis to 0.5 %. In sintered material without any anisotropy, e.g. by deformation, the area fraction is equal to the volume fraction. The assumption that the whole carbon content of 600 µg/g forms W_2C would lead to a volume fraction of 2.1 %. Obviously carbon is additionally present in form of super-solid solution in the tungsten matrix. Another reason of this mismatch could be that small carbide grains are not detected completely by the quantitatve image processing.

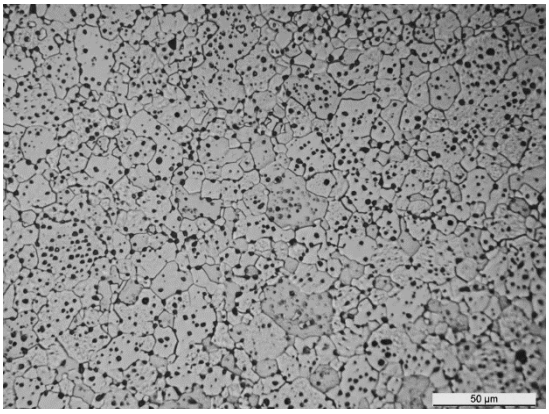


Figure 1: LOM of a metallographic section of WL20C600 in etched condition. The La_2O_3 particles can be recognized as black dots.

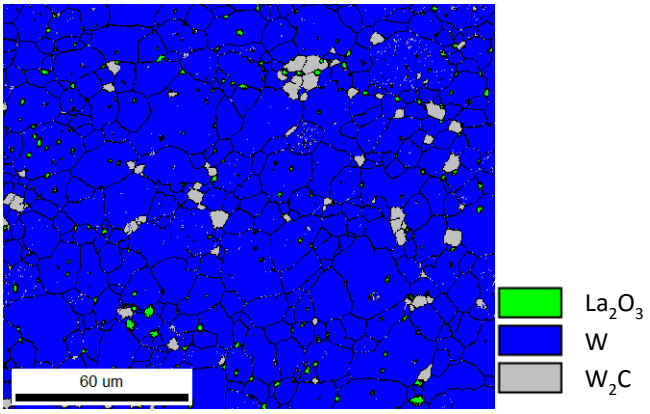


Figure 2: EBSD phase map of WL20C600.

Diffusion Couples

In order to investigate the volume diffusion of the emitter element lanthanum in the tungsten matrix, diffusion couples were prepared. Cylindrical samples (Ø 14 mm) of W, WLZ and WL20C6000 were machined. The length was 35 mm for the W cylinders and 15 mm for the other materials. The diffusion couples were realized by joining the face sides of two different materials by hot pressing (1800 °C, 5 min, 50 MPa). Subsequently, diffusion annealing was performed at 2300 °C for 4 hours in argon atmosphere. From these material composites cylindrical samples (Ø 10 mm, length 20 mm) were cut in such way that the material interface is parallel to the face sides. To study the effect of carbon doping, diffusion couples of the material combinations W / WLZ and W / WL20C6000 were prepared. The tungsten face was reduced to a thickness of 100 µm prior to the measurement.

Material was continuously removed from the face side of the W end of the diffusion couple by sputtering (mask Ø 8 mm) and analyzed by means of glow discharge mass spectroscopy (GDMS). The lanthanum signal obtained from the tungsten volume is a measure for the diffusion of lanthanum into the pure tungsten.

The "Bochum Modell Lamp"

The effect of carbon doping on the burning behaviour of the cathode was studied by highly-instrumented lamp tests in the so called "Bochum Model Lamp". A detailed description of this test facility and the data treatment of the different measuring technologies is available in reference [12, 13]. The relevant monitoring techniques applied for the present study are given in Table 1.

Table 1: Instrumentation of the Bochum Model Lamp relevant for the present study.

Instrumentation	Measured quantity	Sampling
Photodiode	Flickering (normalized time dependent light output)	10 Hz
CCD camera	Thermal image of the cathode surface	1 Hz
Spectrometer	Line profile of the density of La+ ions in the arc close to the cathode tip	1 Hz

Flickering is defined as the variation of the photo current within a time frame of 10 seconds relative to the mean value observed in that time frame. The complex data treatment of the CCD camera signal enables the termination of the cathode tip temperature (T^{tip}) and the optical emissivity [2]. The typical duration of the lamp tests is 8 hours.

Application Test

The performance of different cathode materials was tested in a standard mercury discharge lamp for industrial application with a nominal power of 3.5 kW. The standard duration of the tests was 1500 hours. The relevant quantities for rating the materials and their target values obtained from the performance of thoriated cathode material (WT, W + 1.8 wt.% ThO_2) are listed in Table 2.

Table 2: Quantities for the assessment of the cathode material in discharge lamps monitored for the test duration of 1500 h. The target values are defined by the performance WT cathodes.

Measured quantity	Target WT
Initial radiance compared to thoriated cathodes	> -1 %
Flickering (based on voltage fluctuation)	< 0.4 %
Diameter of the cathode plateau	< 205 %
Electrode gap (measure for burn-back)	< 110 %
Reduction of the integrated light output (Blackening)	> 85 %

The flickering was derived from voltage fluctuation during operation. The value is calculated as the maximum fluctuation observed within a time intervall of 10 minutes relative to the mean voltage in that time intervall. A voltage fluctuation of 0.4 % corresponds to light output fluctuations of approx. 0.7 % in this 3.5 kW tool.

Results

Investigation of Flickering

The performance of cathode materials W, WLZ and WT20 (W + 2 wt.% ThO_2) is compared in Fig. 3 where the tip temperature (T^{tip}) is shown for duration of 8 h in the “Bochum Model Lamp”. Doping the cathode with lanthanum- or thorium-oxides reduces T^{tip} significantly. The emitter effect of lanthania doped tungsten and thoriated tungsten is comparable but the temperature signal of the WLZ cathode shows variation over time that is undesired and linked to flickering. These fluctuations of WLZ cathode were investigated in detail. The data of the different measurement techniques available in the “Bochum Model Lamp” is shown in Fig. 4 for the first 5000 s of the lamp test. The normalized photocurrent (blue line) clearly shows the instability of the light output of WLZ material. At the beginning of the lamp test the burning behaviour is stable and comparable to thoriated cathode material. After approximately 1 h flickering in the magnitude of 5 % can be seen.

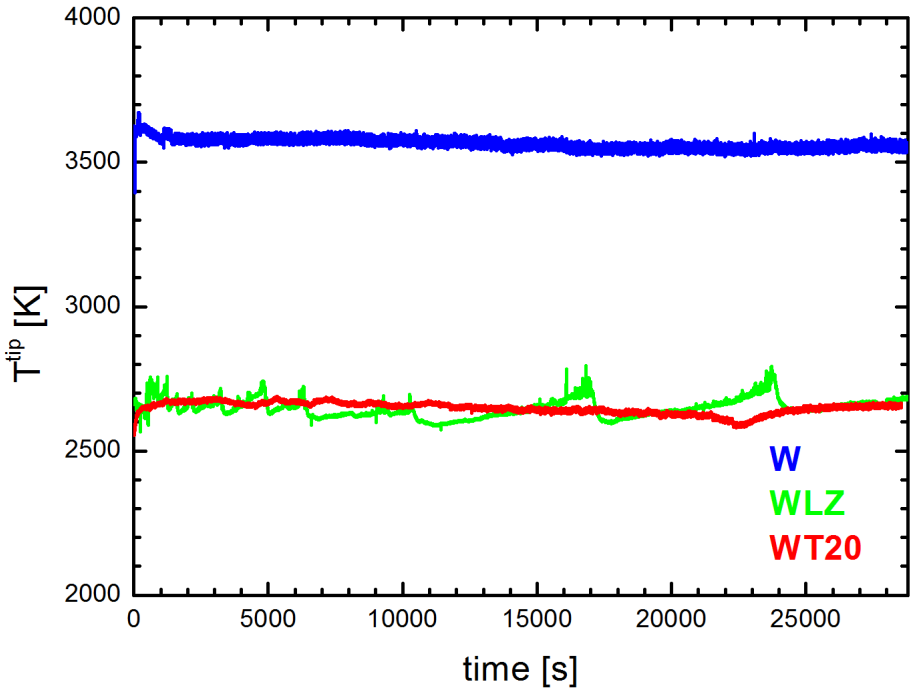


Figure 3: Time-resolved “Bochum Model Lamp” test data obtained from different cathode materials. T^{tip} is shown for the whole test duration of 8 h.

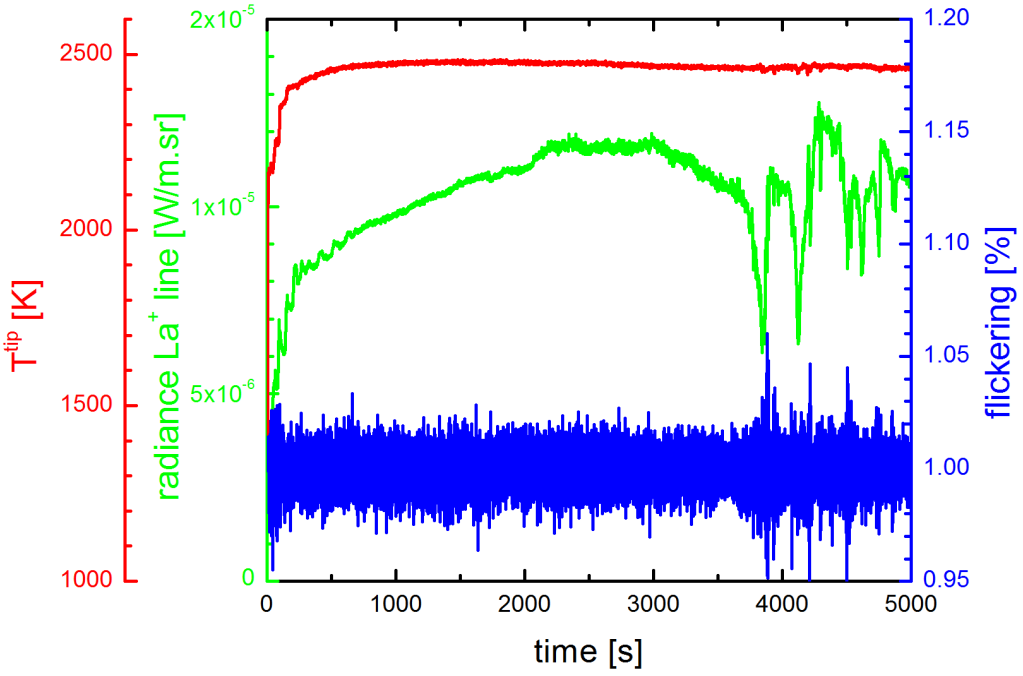


Figure 4: Time-resolved “Bochum Model Lamp” test data obtained from WLZ cathode material. T^{tip} (red), the intensity of the La^+ line close to the tip (green) and the normalized photocurrent (blue) are shown for the first 5000 s of the lamp test.

A first insight to the mechanism of flickering results from observation of the radiance of the La^+ line at 394,91 nm [13]. The intensity of the La^+ line increases continuously at the beginning of the lamp test indicating an increasing density of the La^+ ions in the arc in front of the tip. At this time no significant flickering takes place. After 3000 s the La^+ signal decreases rather quickly followed by the onset of significant flickering events. In between the flickering events the La^+ ions signal recovers.

Additional information about the flickering events is obtained from the images of the CCD camera, see Fig. 5. During the initial stage as shown in the left image (1000 s) a deposit forms approximately 2 mm beyond the tip which is recognized in the temperature image by locally increased spectral radiance (marked by white dashed boundary line) pretending an increased temperature due to increased thermal emissivity. With ongoing burning time the area with deposits increases (see middle picture in Fig. 5). As soon as significant flickering occurs the deposit is partially removed, see the image on the right (3932 s). The arc spot on the tip of the cathode can be recognized in the image taken at 3500 s, see white arrow. The halo at the tip vanishes during flickering because the spot switches to the emitter deposit beyond the cathode tip. The spot follows the emitter deposit and removes it due to evaporation. After consuming the accessible deposit the La^+ ion density in the plasma is re-established and the arc moves back to the tip.

After the lamp test the emitter deposit was analyzed by means of SEM. The back scatter electron image which is sensitive to the atomic number is shown in Fig. 6. The original tungsten surface can be recognized by the light grey. It is covered by a phase appearing in darker grey. The quantification result of energy dispersive X-ray spot analysis (EDS) of this phase (see Fig. 6) shows that the deposit consists of a lanthanum tungstate. From literature it is known that the work function of rare earth tungstates is even lower than those of rare earth oxides [14]. Therefore the arc is attracted by the deposit.

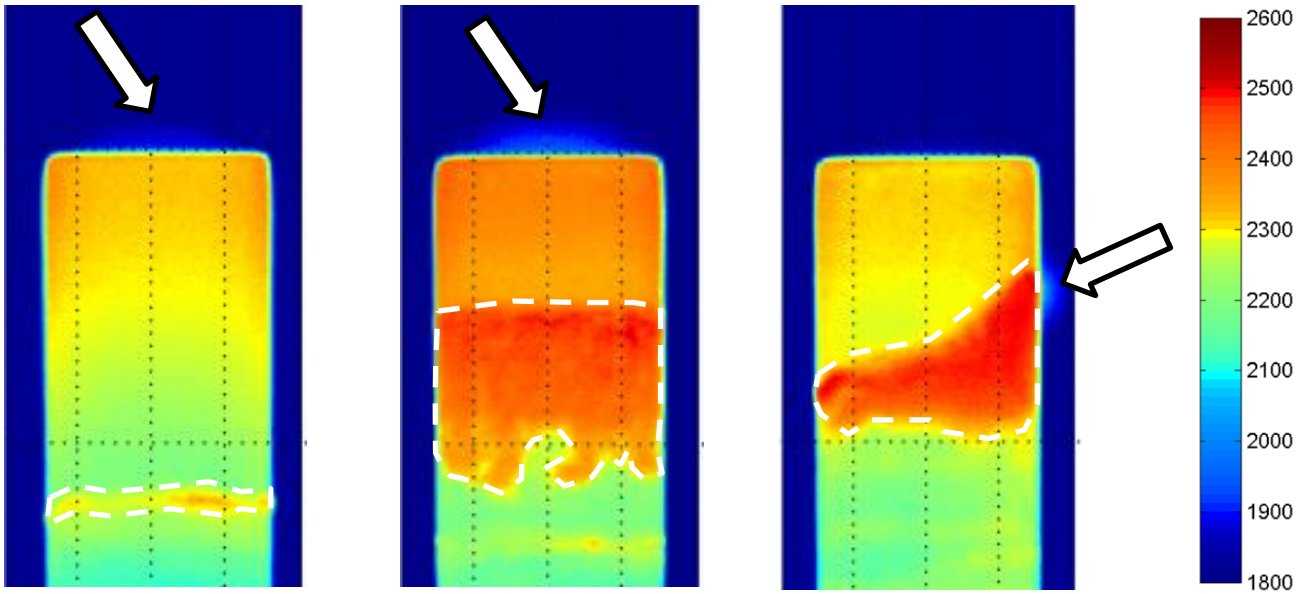
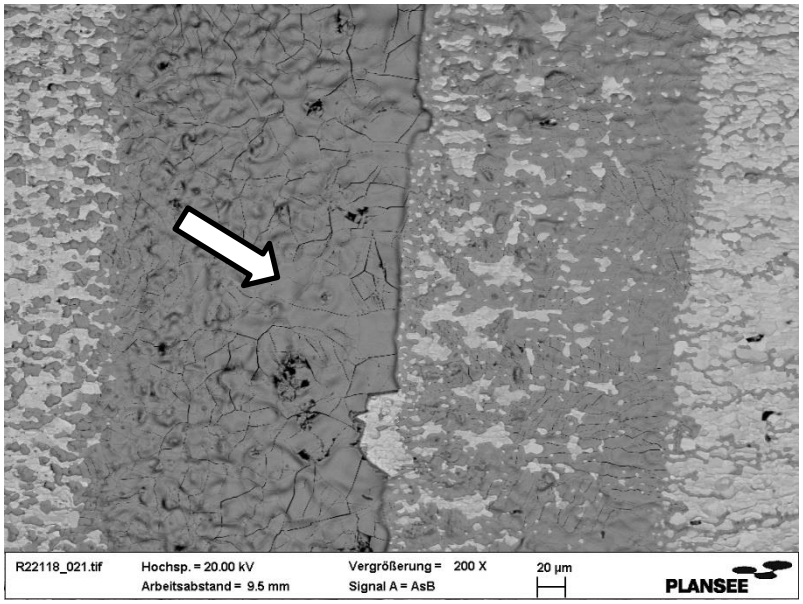


Figure 5: Temperature image of a WLZ cathode at different times. The lamp test data of this cathode is shown in Fig. 4. Temperature determination (K) is based on the emissivity of pure tungsten. A scale for the images is provided by the diameter of cathode which is 1.5 mm. The white arrows indicate the location of the arc spot. The white dashed lines mark the emitter depostis beyond the tip of the cathode.



cathode tip

EDS quantification in at.%:
La 45, O 35, W 20

Figure 6: SEM mass contrast image of the emitter deposit after the lampt test of the WLZ cathode shown in Fig. 4–5. The location of EDS is marked by the white arrow.

Effect of Carbon Doping

The bulk diffusion is studied by GDMS analysis of the interface of diffusion couples. The couples W / WLZ and W / WL20C6000 have been compared to study the effect of carbon doping. The samples have been exposed to a temperature of 2300 °C for 4 h in argon atmosphere in order to activate diffusion. In Fig. 7 the lanthanum signal through the interface is compared for both diffusion couples. In the W / WLZ diffusion couple obviously no remarkable diffusion of lanthanum took place. In contrast the data of the W / WL20C6000 couple shows diffusion of lanthanum into the pure tungsten material. By this result the activation of lanthanum diffusion in tungsten by carbon doping becomes evident.

The effect of the carbon addition on the burning behaviour of the cathode was studied in the “Bochum Model Lamp”. Fig. 8 shows a lamp test with a WL20C600 cathode which was performed with the same parameters as the test of the WLZ cathode shown in Fig. 3. No flickering occurs for the carbon doped material. The intensity of the La^+ line in front of the tip increases at the beginning of the test until a rather stable plateau is reached. The thermal image shows no emitter deposits close to the cathode tip, see Fig. 9. Obviously carbon reduces the thermal stability of the oxidic deposit.

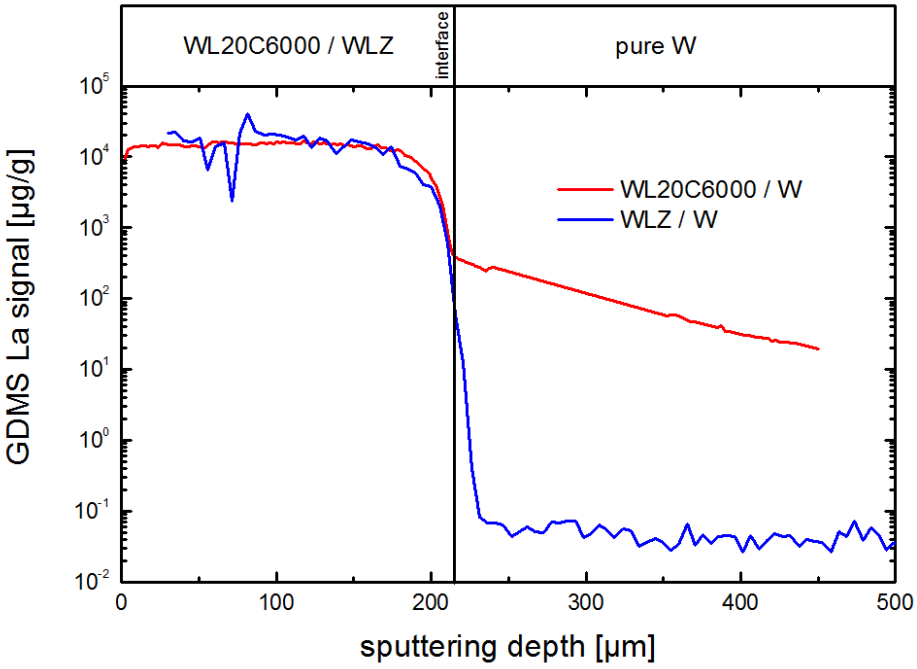


Figure 7: Lanthanum signal of the GDMS measurment through the interface of diffusion couples.

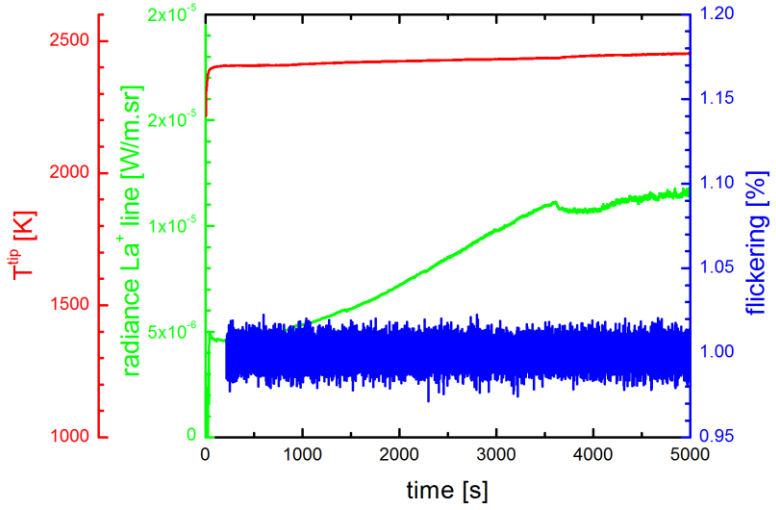


Figure 8: Time-resolved test data obtained from WL20C600 cathode material in the “Bochum Model Lamp”.

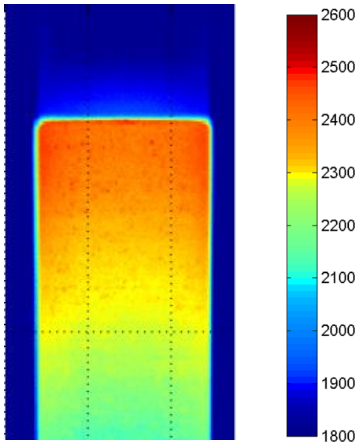


Figure 9: Temperature image of a WL20C600 cathode at 2500 s, for lamp test data see Fig. 8.

Application Test

The voltage fluctuation as a measure for flickering is shown in Fig. 10 for different 3.5 kW standard lamps containing the cathode materials WLZ, WL20C600 and WT. Additionally, the data of a WLZ cathode carburized on the surface close to the tip is shown.

The flickering of the lanthanized cathode (WLZ) cannot be prevented by carburizing the surface of the cathode. The stable voltage of the WL20C600 cathode shows that carbon doping of the whole cathode volume leads to a stabilisation of the burning behaviour comparable to that of the WT cathode. The comparison of the performance of the cathode materials discussed with regard to all target quantities listed in Table 2 is visualized in Fig. 11.

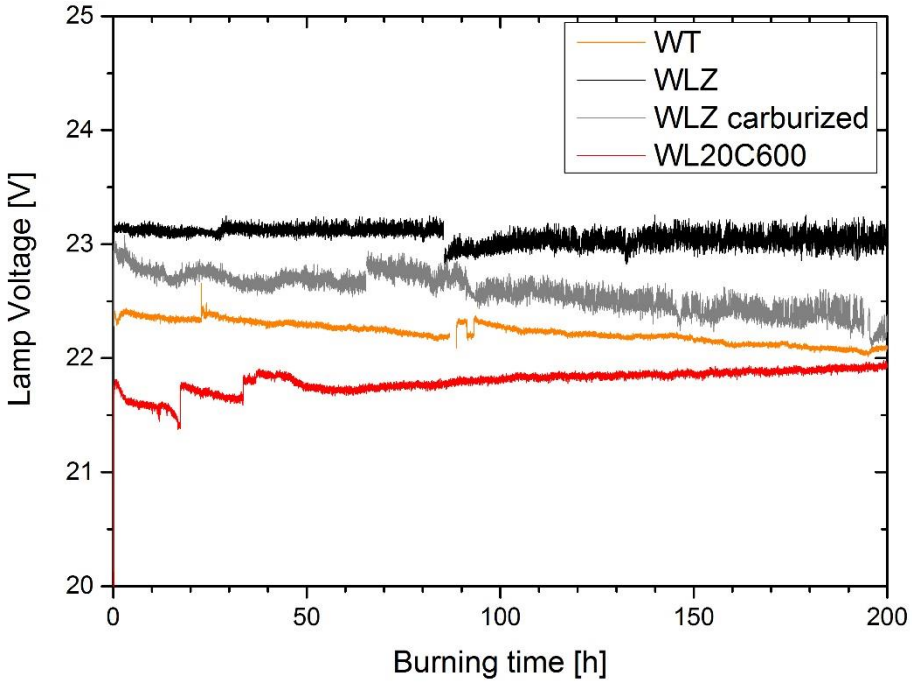


Figure 10: Voltage fluctuation during the first 200 hours of the lamp test as a measure for flickering of 3,5 kW standard lamps containing different cathode materials.

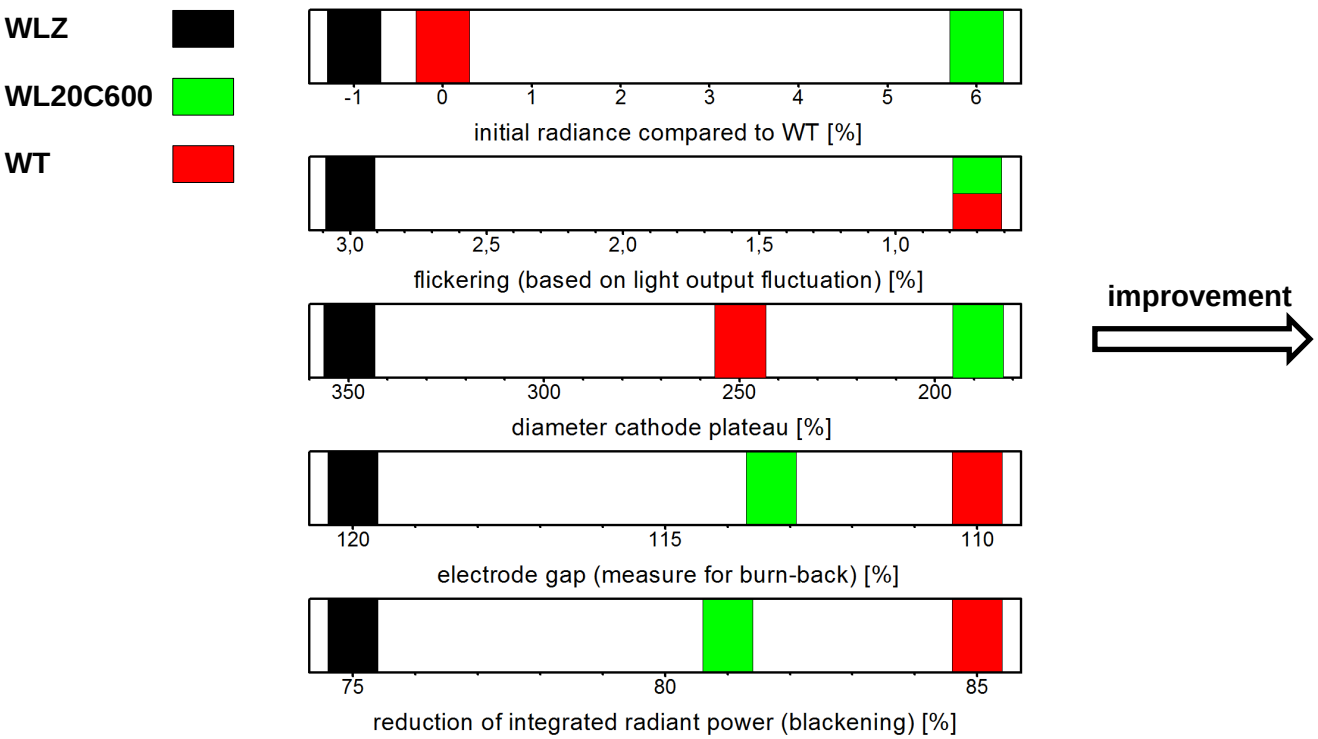


Figure 11: Rating of the cathode materials WLZ (black), WL20C600 (green) and WT (red) for all target quantities regarded for industrial application of a 3,5 kW standard mercury discharge lamp. The scale definition of the individual axes of abscissae enables the visualization of improvement as a shift towards the right side for all target quantities.

The comparison of WLZ and WL20C600 shows that carbon doping is advantageous with respect to all target quantities defined. The WL20C600 cathode is superior with regard to initial light output and shape stability of the plateau of the tip. The thoriated material shows the least blackening and the lowest increase of the electrode distance. Concerning the blackening the analysis of the SEM EDS analysis showed that lanthanum-containing species are deposited on the quartz bulb.

Conclusion

Understanding of Flickering

The fundamental research in the “Bochum Model Lamp” shows that flickering events from lanthanum doped cathodes are triggered by depletion of the emitter concentration in the arc spot close to the tip. Since the work function reducing lanthanum monolayer is the dynamic balance of evaporation and redeposition from the plasma it is assumed that the decrease of the La^+ concentration in the plasma coincides with the partial decomposition of the monolayer. The consequence is an increase of the work function at the cathode tip. Obviously the decrease of the La^+ concentration at the tip is caused by condensation of lanthanum tungstates with low work functions beyond the tip. The consequence is a temporary switch of the arc spot from the cathode tip to the emitter deposit below the tip. The emitter deposit evaporates leading to a recovery of the La^+ concentration at the tip and finally to the return of the spot to the tip.

Effect of Carbon Doping on Flickering

Concerning the elimination of flickering by carbon doping two mechanisms could be identified. Firstly, carbon enhances the volume diffusion of the emitter substance lanthanum. Therefore the depletion of the emitter at the cathode tip is prevented. Secondly, the presence of carbon avoids the formation of emitter deposit with low working function close to the tip as observed for lanthanized cathodes without carbon doping. These effects lead to a stable arc attach at the tip.

Application to Industrial Lamps

The results obtained from testing industrial lamps confirm that carbon doping of the material prevents flickerning. Obviously the increased volume diffusion of lanthanum is essential since carburation of the surface only is not effective. The drawback of WL20C600 compared to WT is mainly the increased blackening and the slightly higher burn back. Since blackening is linked to condensation of lanthanum containing species at the bulb it is assumed that the increased blackening is a consequence of the enhanced volume diffusion of lanthanum. The increased burn back could be linked to the reduced high temperature strength of the phase W_2C compared to pure tungsten. This assumption is based on the fact that the melting point of W_2C is lower compared to pure tungsten.

Summary

Fundamental research allows a comprehensive understanding of the positive effect of carbon with regard to the prevention of flickering. Carbon doping enhances the diffusion of lanthanum in the tungsten matrix and avoids lanthanum containing deposits beyond the tip. For both reasons the light output is stabilized. Based on that research an industrial production process for the new carbon doped cathode material WL20C600 was developed. The beneficial effect of carbon with respect to flickering has been demonstrated by comparing the burning behavior of industrial short arc lamps equipped with WLZ and WL20C600 cathodes. With regard to flickering the carbon doped material WL20C600 performs significantly better than WLZ and even comparable to thoriated cathode material. The main trade-off observed for WL20C600 is the increased blackening which is caused by increased emitter evaporation from the cathode and its condensation at the quartz bulb.

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