Design, development and performance of a new solid mercury dispenser for fluorescent lighting

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1. Introduction
The trend of minimizing the environmental impact of end-of-life fluorescent lamps leads to increasingly stringent regulations on the use of mercury for fluorescent lamps. The directive 2011/65/EU of the European parliament and the council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment states that the maximum Hg content of fluorescent lamps with a power < 30W decreases from 5 mg before the end of 2011 to 2.5 mg from the beginning of 2013.
As a result, the industry is shifting from liquid mercury dosing to more reliable, solid Hg dispensing solutions. For compact fluorescent lamps (CFLs), this transition was concluded for the most part, while it is still ongoing for tube lamps (TLs).
Older mercury dosing techniques employed glass or metal capsules to be mounted in the lamp and opened after lamp sealing, increasing lamp complexity and production cost. In recent years, solid mercury dispensing systems are used but they also have disadvantages. Titanium mercury alloy strips, although less complex than capsules, also have to be mounted in the lamp and activated near 900 °C after lamp sealing [1]. Porous iron or glass/ceramic pellets containing liquid mercury require different production steps, and may damage the lamp coating. One of the most prominent examples is ZnHg50, the pellets have the advantage of combining a low complexity with easy dosing in the lamp [2]. However, the mercury contained in the alloy needs to be set free through heating of the pellet, with a risk of mercury reabsorption at ambient temperatures during prolonged lamp downtimes. Moreover, the Zn level in the activated mercury causes the vapor pressure to drop below that for pure mercury.
In the search for a Hg dosing solution that combines the easy handling of a solid amalgam pellet with the immediate availability of liquid mercury, novel SnHg50 pellets were developed. These contain pouches of liquid mercury, which are created in-situ during pellet production. The present paper will discuss the design, development and lamp performance related properties of these SnHg50 pellets.

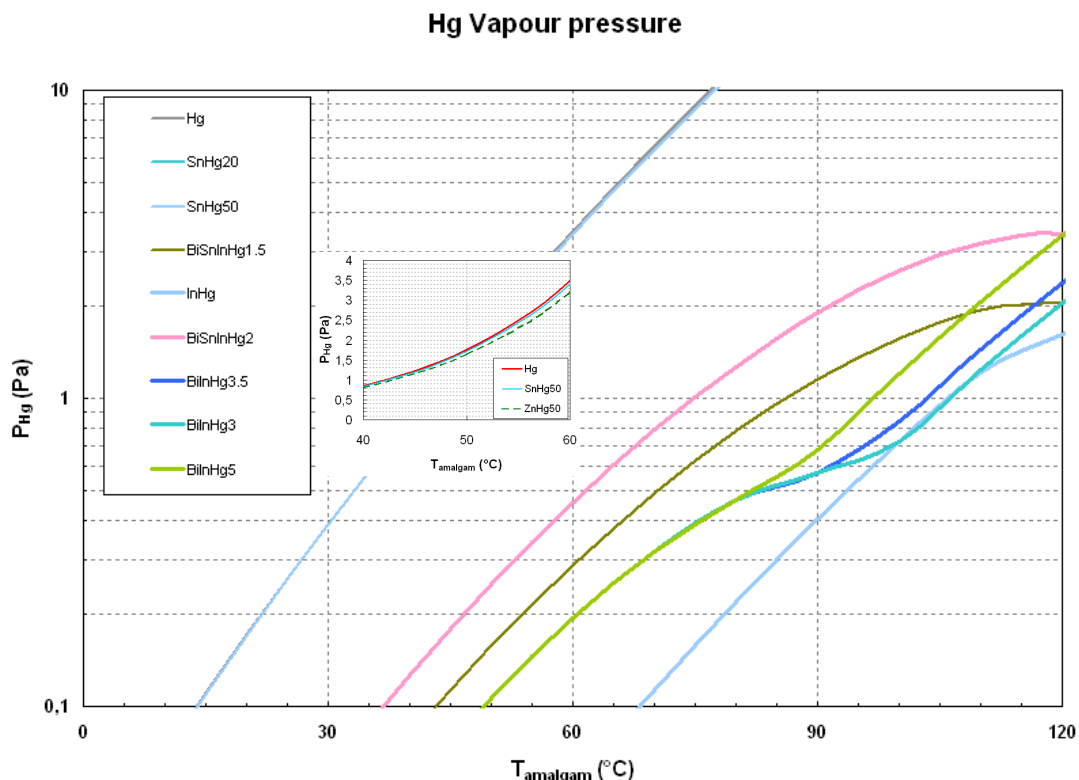## 2. Design of improved mercury dispenser
For the design of an improved solid mercury dispenser, the mercury vapor pressure of different amalgams as a function of temperature was calculated by means of the Factsage package (Figure 1). This database computing system for chemical thermodynamics consists of a series of calculation modules accessing various pure substances and solution databases, which are developed based on optimized literature data [3]. The results show that the Hg vapor pressure as a function of temperature of SnHg50 approaches that of pure mercury, and is higher than the vapor pressure of ZnHg50. The reason for this can be found in the Sn-Hg phase diagram (Figure 2), indicating that above -8 °C about 40 wt% of the alloy consists of a liquid phase. This liquid phase is mercury with a small percentage of dissolved Sn, for which the vapor pressure is nearly identical to that of pure

mercury. Therefore, the behavior of such an alloy in the lamp will be comparable to that of a hollow or porous pellet with mercury-filled cavities.

By means of the Factsage package, the equilibrium phase formation at 10 mbar was calculated for SnHg50 and ZnHg50 at 10 mbar (7.5 torr) and temperatures between 0 and 400 °C (Figure 3). The curves show that SnHg50 consists for about 40 wt% of a liquid phase, both at lamp operating temperatures and at room temperature. This means that the liquid mercury available for vapor generation during operation remains available in liquid form during lamp downtime and storage. The ZnHg50 on the other hand undergoes a phase transformation at 38 °C, where the alloy moves from a completely solid sphere to one that contains about 50 wt% liquid phase. After cooling below 38 °C, e.g. during lamp downtime, a thermodynamic drive for the system exists to return to a complete solid phase. In this way, the Hg will not be available in liquid form and would require time after lamp start-up to be retransformed again, leading to a longer run-up time for the ZnHg50 pellet. Due to its phase stability over the temperature range between room temperature and operating temperature, there is no such phase transformation required for SnHg50.

In order to deploy the SnHg50 alloy in lamp manufacturing, a number of conditions should be fulfilled. First, the liquid mercury should be well contained inside the pellet, and be released only once inside the lamp. During handling, the pellet should behave like a fully solid sphere, ensuring reliable and consistent dosing at high manufacturing speeds. Furthermore, size and roundness of the amalgam sphere must be controlled and must fit within tight error margins.
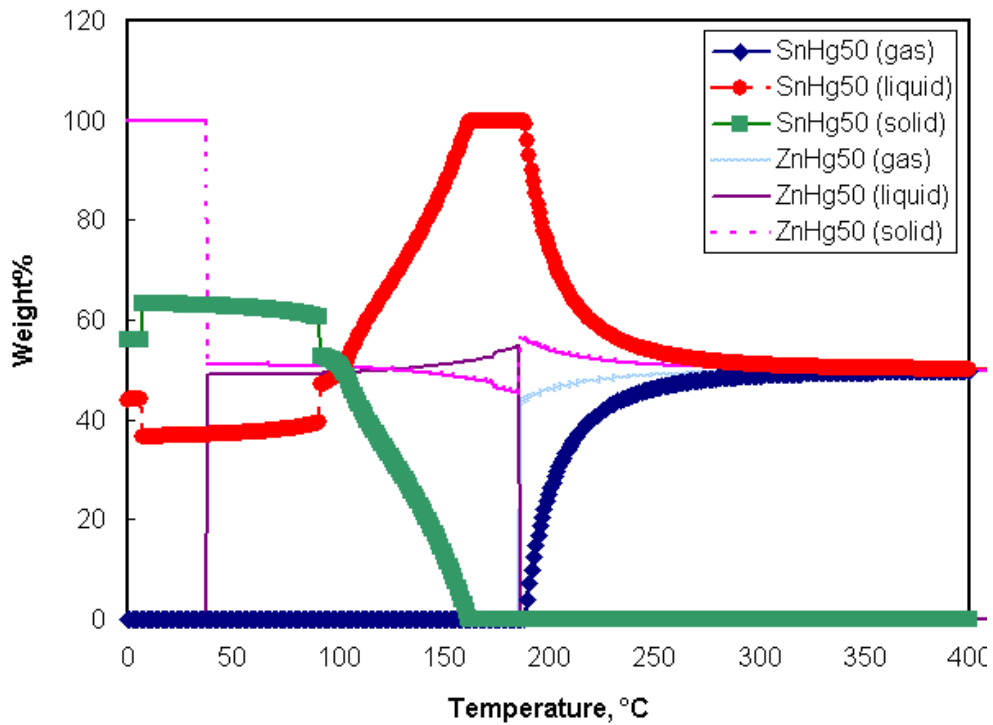
The following section will discuss how these conditions were met through the development of a suitable production process for SnHg50 spheres.
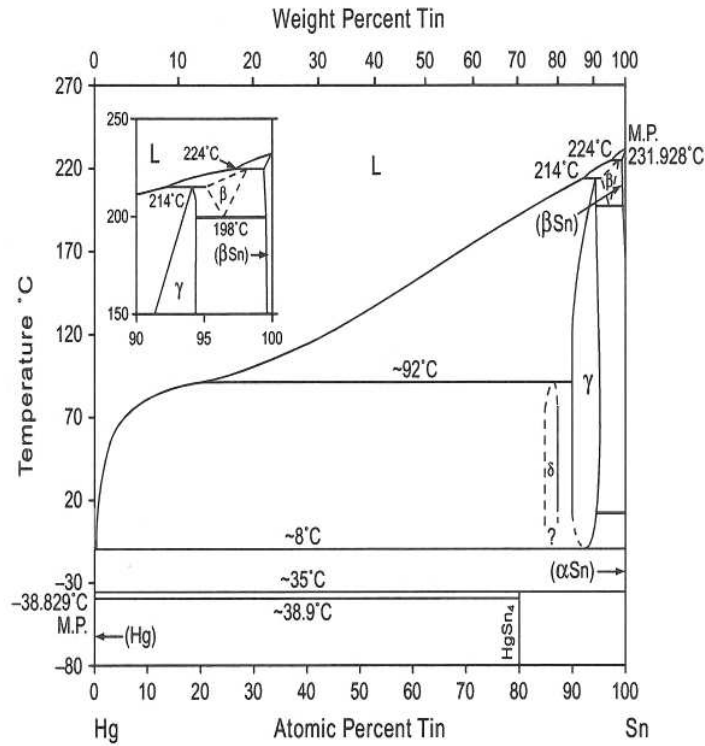
Figure 2: Phase diagram of the Sn-Hg system (redrawn from [4]).

Figure 3: Phase formation as a function of temperature at 10 mbar (7.5 torr) for SnHg50 and ZnHg50 (Factsage calculations)

3. Realization

In order to meet the strict requirements for the SnHg50 pellets, a new production process was developed. This process makes use of the surface tension of the liquid melt, which transforms irregularly shaped alloy droplets into spheres to reduce the surface tension. A liquid melt jet is cut directly into droplets of appropriate volume, which are allowed to spheroidize and solidify in a suitable cooling medium.
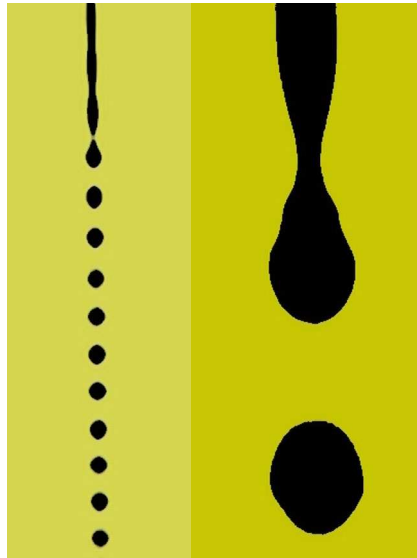
Figure 4: Stroboscope lighted image of the cutting of a melt stream in monosized droplets.

The mechanism of cutting the liquid stream is shown in Figure 4 for two different magnifications. The final sphere diameter in this image is 800 µm. The melt stream is produced using a nozzle. Vibrations are used to generate defined necking positions in the melt stream. These neckings are enlarged by the surface tension of the liquid metal. Finally, the neckings lead to a "break-off" of single droplets, which can form a perfect sphere, provided all conditions are well optimized. Obviously, the main advantage of this production method is that the amalgam pellet is produced directly from the melt.

The basic principle of cutting down a liquid stream in single droplets has been known for over 100 years. Lord Rayleigh described the fundamentals already in 1879 [5]. The basic principles of the break-down of the melt jet are described in [6,7]. However, developing the principle into a mass-production tool for a solid amalgam containing liquid-filled cavities requires specific expertise.

The size of the amalgam spheres can be controlled by the cutting frequency f (i.e. the production rate of the droplets), as described by following formula:

$$f = \left(\frac{8 \cdot \sigma}{\rho \cdot (0.529 \cdot d)^3 \cdot 4.5^2} \right)^{\frac{1}{2}} \qquad (1)$$

where d is the sphere diameter (m), σ the surface tension of the melt (N/m) and ρ the density of the melt (kg/m³). As surface tension and density are given material properties, this equation shows that there is a strong relation ($f \sim d^{-3/2}$) between sphere diameter and cutting frequency. This implies that the process can be tuned to produce smaller spheres, which allows meeting future restrictions on total mercury loading in fluorescent lamps. The basic production process is followed by sorting steps, which assure a high consistency in size and roundness. Accurate process control during dropping enables a process yield larger than 90% after sorting.

After sorting, the spheres are coated with a powder (European patent EP 2 145 028 B1). The coating step results in a dense coating layer around the initial SnHg50 sphere, which prevents the presence of liquid Hg at the surface. After coating, the spheres behave like individual particles that can be easily singulated in the exhaust machine.

4. Characterization

A light optical image of the SnHg50 spheres is given in Figure 5, illustrating the high consistency in size and roundness. The spheres are free flowing.

Figure 5: Light optical image of SnHg50 spheres with a Hg content of 1.5 mg.

The internal structure of the SnHg50 amalgam was visualized by means of X-ray microtomography, allowing the construction of 2-D slices and 3-D images based on the different X-ray absorption of phases with different atomic number [8]. The left side of Figure 6 shows a 2-D slice of a SnHg50 amalgam sphere. The bright zones correspond to the Hg-rich liquid phase, where X-ray absorption is high. The darker areas are the solid Sn-rich phase.

This image confirms the success of the design goal of in-situ production of a quasi-solid dispenser system with liquid mercury contained in cavities inside the amalgam sphere. It can also be seen that the outer shell of the sphere is fully solid, which explains its excellent rolling behavior. The presence of a fully solid outer shell is confirmed by optical microscopy (Figure 5) and SEM (right side of Figure 6).
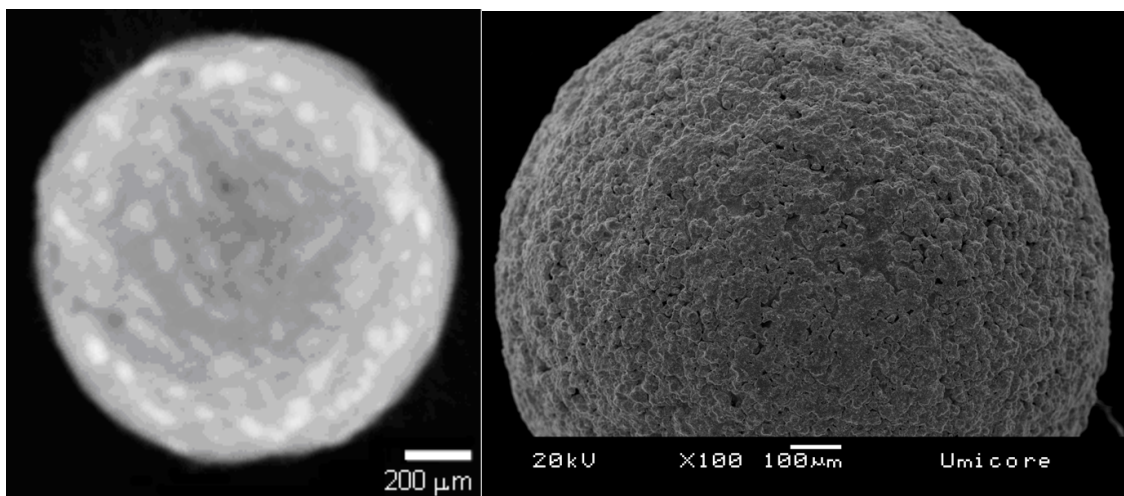

Figure 6: Left: 2-D slice of a microtomography scan of a SnHg50 amalgam sphere at the maximum diameter. Right: SEM image (secondary electrons) of a SnHg50 amalgam sphere.

In order to simulate the activation of the SnHg50 in the lamp and to compare it with the behavior of ZnHg50, a thermogravimetric analysis (TGA) was performed on both materials under a pressure of 0.1 mbar (Figure 7). During this test, the mass loss of each amalgam was recorded, while the temperature was increased at a rate of 0.83 °C/s. The mass loss observed in Figure 7 is related to the evaporation of Hg from the amalgam. Under the applied conditions, the mass loss or evaporation for the SnHg50 starts around 75 °C, and reaches a plateau around 200 °C. For ZnHg50 on the other hand, the mass loss starts around 200 °C, leveling off around 260 °C and reaching a 45% mass loss at 300 °C. This implies that during activation of ZnHg50 in the lamp, a higher temperature and/or a longer holding time at high temperature is required to release Hg. In the Figure 3 the heat supplied in the TGA experiment for ZnHg50 is first consumed by the phase formation at 38 °C, which melts half of the alloy. Afterwards the additional heat results in Hg evaporation which leads to the observed delay. SnHg50, on the other hand, already consists of ~ 40 wt% of liquid phase, allowing a fast start of evaporation. In conclusion, the Hg during heating is much faster for SnHg50 than for ZnHg50.

Figure 8 shows SEM images of the SnHg50 amalgam sphere after the TGA experiment. After the Hg release, the geometry of the sphere remains intact, however, with a very rough surface that contains holes. These holes are created by the evacuation of the liquid Hg from the interior of the amalgam sphere.
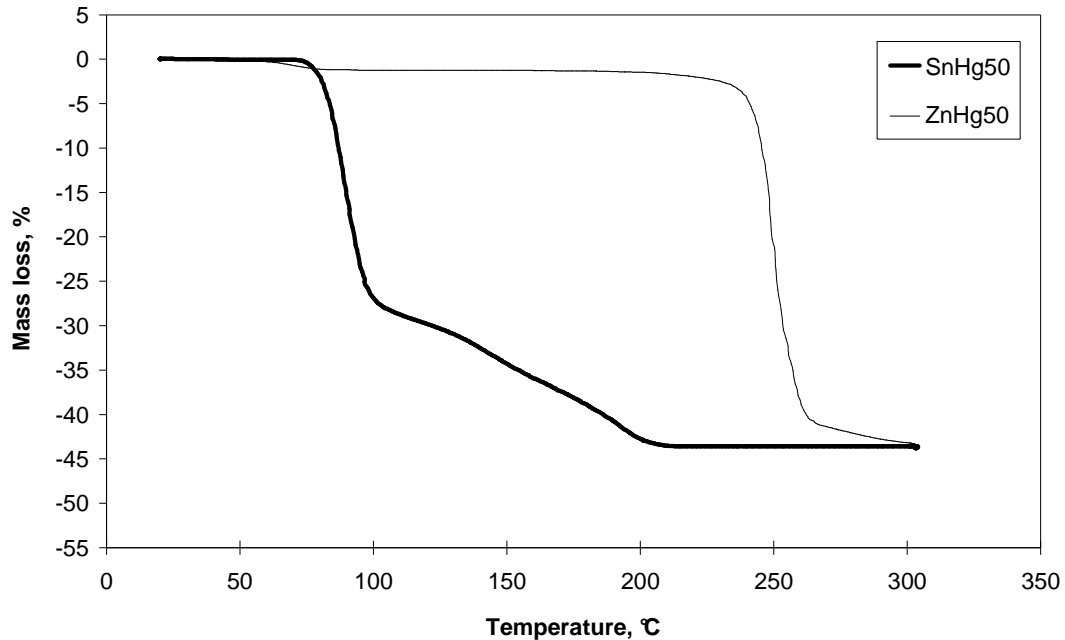
Figure 7: Thermogravimetric analysis (TGA) curves for SnHg50 and ZnHg50 at 0.1 mbar and a heating rate of 0.83 °C/s.
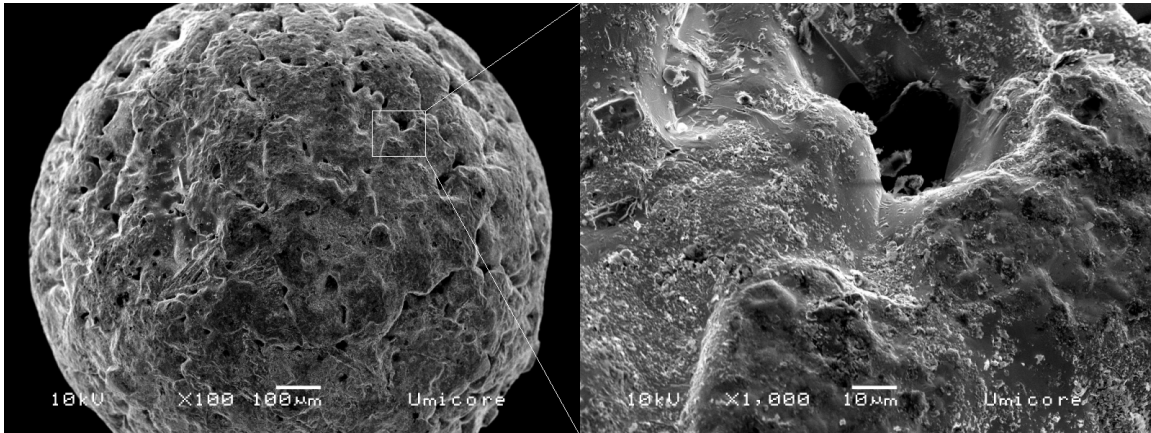
Figure 8: SEM images of the SnHg50 amalgam sphere after the TGA experiment (after Hg evacuation)

5. Conclusion

An improved Hg dosing solution was developed in the form of novel SnHg50 spheres. These combine the easy handling of a solid amalgam pellet with the immediate availability of liquid mercury in the whole range between room temperature and lamp operating temperature, as illustrated by the phase diagram and Factsage modeling. This liquid phase ensures a mercury vapor pressure higher than the one for ZnHg50, and only just below that of pure Hg. TGA measurements, simulating the activation process, showed that the SnHg50 spheres release Hg vapor at a higher rate and a lower temperature than ZnHg50 spheres.

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For the production of these spheres an efficient process was developed, based on the surface tension of the melt, resulting in highly round and homogeneous SnHg50 spheres. The spheres handle like solid spheres, with excellent flowability, allowing high lamp manufacturing speeds. The process is flexible in terms of sphere size, and allows for the evolution towards smaller spheres with reduced total Hg content, in order to comply with future restrictions on Hg loading in fluorescent lamps.

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