Korean J. Chem. Eng., **22**(6), 905-909 (2005)

Manufacturing Process of Self-Luminous Glass Tube Utilizing Tritium Gas: Experimental Results for DB Construction

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(*Received 18 March 2005 • accepted 30 June 2005*)

Abstract–As the first step of Self-luminous Glass Tube (SLGT) mass production and DB construction, the characterization and the optimization of a phosphor coating were attempted by using a cathodoluminescence (CL) device. The experiment was divided into three parts: measurement of the relative luminance at various exciting conditions, measurement of the absolute luminance at 4 keV, and a degradation experiment. The relative luminances were measured at various conditions with different phosphor thicknesses, energies and current densities. Regardless of the energies, as the current density increased, and the thickness decreased, the relative luminance increased. The absolute luminance was measured at only 4 keV. Absolute luminance at other energies was estimated from relative luminance data by using a conversion factor calculated from absolute and relative luminance measured at 4 keV. We tried to estimate the expected life of SLGT, which is limited by the reduction of the phosphor efficiency and the amounts of tritium, by additional degradation experiments under severe conditions. The luminance of a 10 μm film was much higher than that of a 20 and 45 μm at the initial stages. On the other hand, the decreasing rate of the luminance at 10 μm was more drastic than that of a 20 and 45 μm. We could see burnt-out spots only on the 10 μm samples. The other samples (20 and 45 μm) were not showing any burnt-out spots.

Key words: Luminance, SLGT, Cathodoluminescence Device (CL), Phosphor, Tritium

INTRODUCTION

From the Wolsong Tritium Removal Facility (WTRF) whose construction work began in February, 2003, 5-7 [MCi] (1 Ci=3.7×10^{10} Bq) of tritium (^{3}H, T) will be produced annually starting from late 2005. Thus, domestic researches related to tritium can be performed more actively [Kim et al., 2002, 2004]. Hydrogen isotopes of protium (H), deuterium (D) and tritium (T) have the same number of protons but a different number of neutrons in the nucleus and as a result, they have different atomic masses and physical properties. Natural hydrogen comprises of 99.958% protium and 0.015% deuterium.

Tritium emits beta rays, which are streams of electrons, with 0-18.6 keV (5.7 keV in average) energies and 12.323 years of half-life, as shown in Eq. (1).

$$T \rightarrow {}^3He^+ + \beta^- + \nu e + 18.6\ keV \qquad T_{1/2} = 12.323 \pm 0.004\ years \qquad (1)$$

The electrons in beta rays collide with phosphor to produce light so that the tritium sealed in phosphor coated glass tubes can make the tubes glow without an external supply of energy [Chung et al., 1994: Kim et al., 2001]. The light emission mechanism can be explained in three steps: excitation of an activator by an external energy source (β-ray), relaxation of the excited activator, and an emission of light with the energy level, returning to the ground level. These

Fig. 1. Application of self-luminous glass tubes using tritium.

SLGT (Self-luminous Glass Tube) can be applied to signs or a compass as shown in Fig. 1 [Bingle et al., 2002; Caffarella et al., 1980; McNair et al., 1991; South, 1997].

Our project is to accomplish two aims. Our first aim is to develop technologies for the SLGT mass production of two commercialized products, which were already chosen as our target, through a characterization and optimization. The second aim is to develop a semi-empirical simulation model by constructing DB using the technologies developed to accomplish the first aim. With this model, the development of a new product with different geometric dimensions and tritium amounts will be easier and more prompt.

And also, the luminances were measured at various conditions

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Table 1. Calculation of each current density for the two-type samples

Type \ Items	T amount (Ci)	Coating area (cm^2)	T amount per unit area (Ci/cm^2)	β-ray flux (Bq/cm^2)	Current density (nA/cm^2)
A	0.009	0.18369	0.0490	1.813×10^9	0.2904
B	7.2	108.87	0.0661	2.447×10^9	0.3920

under different phosphor thicknesses, energies and current densities. On the other hand, as we can estimate an expected life of SLGT limited by its phosphor efficiency and tritium reduction by additional degradation experiments under severe conditions, we performed basic research on degradation experiment. With the results of the luminance measurement, the degradation of phosphor will be also discussed.

EXPERIMENTAL

As the first step of SLGT mass production and DB construction, the characterization and optimization of the phosphor coating were attempted by using a cathodoluminescence (CL) device, which has the same principles as the luminance of SLGTs. Since we are planning to make two different types of products (Type A and B), we selected an Auger gun based on the calculation as shown in Table 1. All the experiments were performed with the electron gun controllable to a few nA.

The β-ray emitted from tritium decay is an electron flow, and the energy is a little high (range: 0-18.6 keV, average energy: 5.7 keV); however, the current densities in our products are very low, as shown in Table 1. As a commercialized CL device could not meet the experimental conditions, we modified the CL device lowered to 0.5 nA/cm^2, corresponding to the lowest density to measure the luminance at 2 keV. And also, due to a financial problem, a difficulty in the experimental set up, and in continuous applications, we did not set up the measuring system of an absolute luminance with the main CL device [Abrams et al., 2000; Hillie and Swart, 2001; Igarashi et al., 2001; Oosthuizen et al., 1997]. Instead, a relative luminance was measured as follows. Photons received at the detector are amplified at PMT, converted into a current, and then the value is shown at each wavelength. As a result, the luminance does not have any units, and also should be different from an absolute one. However, as the measuring method and device are relatively simple, we measured the relative luminance for all the samples instead of the absolute luminance. Then we measured an absolute one for only a few samples, and found a conversion factor from the two values. The absolute one corresponds to an actual luminance, and the value can be expressed in Lamberts.

As we already explained in our previous paper in detail [Kim et al,, 2005, submitted], the CL device was equipped with an Auger gun as an electron source, a measuring system to display the CL spectra, a vacuum system, and a feedthrough to measure the current applied to the samples. Five samples were loaded at a time, and the samples were prepared by screen printing (size: 10 mm×10 mm) onto an ITO plate (size: 20 mm×20 mm) as shown in Fig. 2 [Kim et al., 2005; Son et al., 2004]. The material of the holder is SUS 304, and the contact resistance was minimized by pressing the ITO plate closely to the holder. The contact resistance was kept constant by using a thin metal film. The current applied to a sample was measured with a multimeter [Abrams et al., 2000; Hillie and Swart, 2001; Igarashi et al., 2001; Oosthuizen et al., 1997].

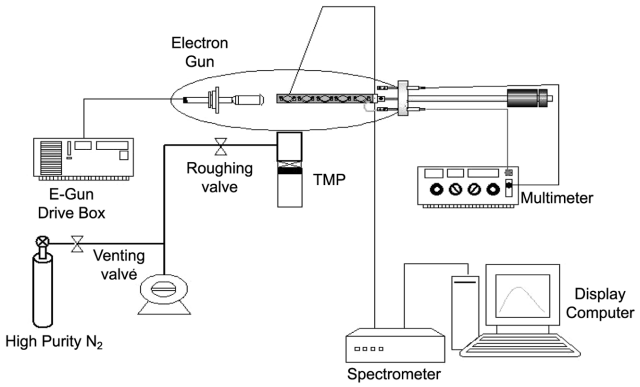

Fig. 2. Cathodoluminescence (CL) device.

Table 2. Experimental conditions

Coating thickness \ Items	10, 20, 45, 60, 100 μm
Drying conditions	Temp: 130 °C, Time: 30 min (in convection oven)
Calcination conditions	Temp: 580 °C, Time: 30 min (200 mL/min with air purge)
Energy and current density	2 keV, 4/3/2/1/0.5 nA/cm^2 4 keV, 4/3/2/1/0.5 nA/cm^2 6 keV, 4/3/2/1/0.5 nA/cm^2 8 keV, 4/3/2/1/0.5 nA/cm^2

The relative luminance of the each phosphor film (thickness: 10, 20, 45, 60, 100 μm based on commercial products) was measured at a given energy with a varying electron flux. The other detailed conditions are shown in Table 2. On the other hand, the absolute luminance was measured at 4 keV with various current densities and thicknesses.

RESULTS & DISCUSSION

1. Measurement of the Relative Luminance at Various Exciting Conditions

As mentioned in Table 2, the relative luminance was measured at various conditions to construct DB. However, only a few results are shown here. The relative luminance at a constant voltage of 6 keV with varying coating thicknesses and current densities is shown in Table 3, and also the results are represented in Figs. 3 and 4. As shown, we observed the same tendency regardless of the energies. As the current density increased, and the thickness decreased, the luminance increased. Therefore, the highest luminance was observed at 10 μm and 4 nA/cm^2. This means that the number of excited photons increased at a higher current density under the same energy, and also, an increased number of photons could pass through the

Table 3. Relative luminance at various coating thicknesses and current densities (at 6 keV)

Thickness (μm) \ Current density (nA/cm^2)	0.5	1	2	3	4
10	1.72E-03	2.83E-03	2.91E-03	3.40E-03	4.40E-03
20	8.44E-04	1.39E-03	1.51E-03	1.80E-03	2.31E-03
45	4.89E-04	6.87E-04	7.15E-04	6.28E-04	1.09E-03
60	4.58E-04	6.01E-04	6.62E-04	6.90E-04	1.06E-03
100	3.83E-04	4.96E-04	5.61E-04	6.10E-04	9.87E-04

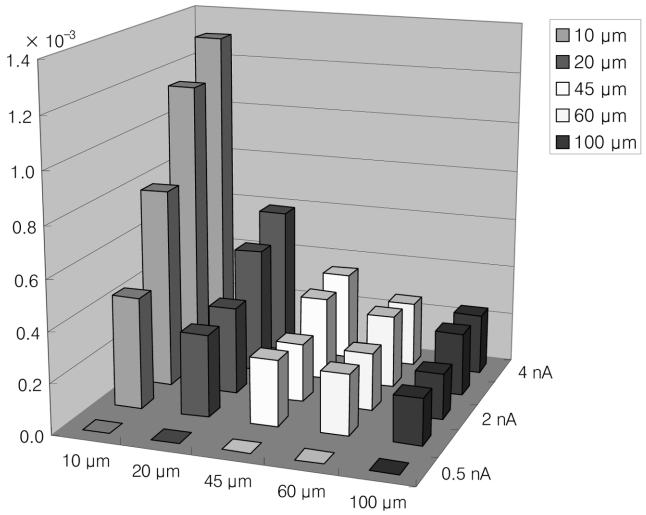

Fig. 3. Relative luminance at various thicknesses and current densities (at 2 keV).

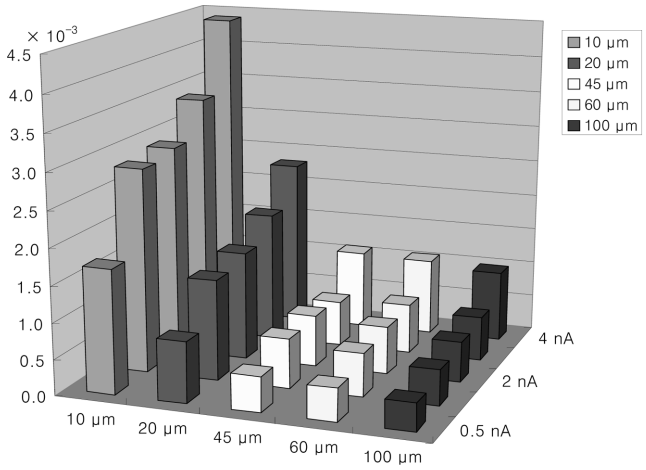

Fig. 4. Relative luminance at various thicknesses and current densities (at 6 keV).

thinner coating.

The relative luminances at a constant current density of 0.5 nA/cm^2 with varying coating thicknesses and energies are shown in Table 4. Although the CL could be observed by the naked eyes at 2 keV and 0.5 nA/cm^2, the luminous peak could not be measured because the luminous spectra were covered with noise. The relative luminances were measured at a 20 μm thickness and 4 keV with varying current densities. The luminances at 0.5 nA/cm^2 which are very close to the current density of the commercialized products, were displayed on a graph as shown in Fig. 5. The maximum luminance was observed at 6 keV, which is very close to the average energy (5.7 keV) of the β-ray from tritium. The luminance was increased as the irradiated energy was increased to 6 keV, and then it decreased suddenly at 8 keV. Although this phenomenon has not yet been properly investigated, we assume that the sputtering of the sulfur atoms by incident electrons might be one of the possible explanations based on previous research. We will try to establish this phenomenon through additional experiments.

Table 4. Relative luminance at various energies and thicknesses (at 0.5 nA/cm^2)

Thickness (μm) \ Energy (keV)	2	4	6	8
10	N/A	2.96E-04	1.72E-03	1.01E-03
20	N/A	2.24E-04	8.44E-04	5.82E-04
45	N/A	1.84E-04	4.89E-04	3.50E-04
60	N/A	1.54E-04	4.58E-04	3.53E-04
100	N/A	1.41E-04	3.83E-04	3.42E-04

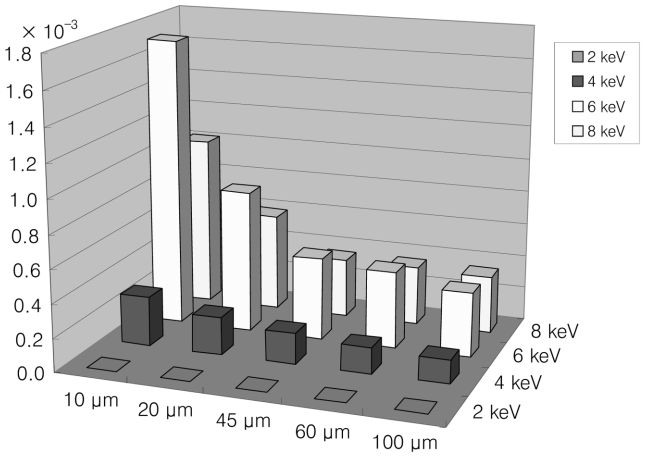

Fig. 5. Relative luminance at various voltages and thicknesses (at 0.5 nA/cm^2).

2. Measurement of the Absolute Luminance at 4 keV

As the relative luminances showed the same tendencies at different energies, we measured an absolute luminance at only one energy state. The relative and absolute luminances at 530 nm, a maximum luminous peak, were measured, and the results are shown in Table 5. The relative and absolute luminance at 4 keV were co-related, and we were able to establish a converting factor from the two values. The relationship of these two values is represented in Eq. (2).

$$\text{absolute luminance (cd/m}^2\text{)} = \text{relative luminance} \times 2{,}332 \quad (2)$$

Table 5. Comparison of the relative and absolute luminance (cd/m^2) at 4 keV

Thickness (μm) \ Current density (nA/cm^2)		0.5	1	3	3	4
10	Relative	2.96E-04	1.34E-03	1.85E-03	2.17E-03	3.71E-03
	Absolute	6.89E-01	3.12E+00	4.30E+00	5.06E+00	8.65E+00
20	Relative	2.24E-04	7.45E-04	8.65E-04	1.17E-03	1.83E-03
	Absolute	5.21E-01	1.61E+00	1.92E+00	3.02E+00	4.46E+00
30	Relative	1.84E-04	3.84E-04	4.06E-04	4.95E-04	7.82E-04
	Absolute	4.28E-01	8.94E-01	9.47E-01	1.15E+00	1.82E+00
40	Relative	1.54E-04	3.56E-04	3.99E-04	4.94E-04	7.79E-04
	Absolute	3.59E-01	8.30E-01	9.30E-01	1.15E+00	1.82E+00
50	Relative	1.41E-04	2.82E-04	3.42E-04	3.55E-04	5.84E-04
	Absolute	3.28E-01	6.56E-01	7.97E-01	8.27E-01	1.36E+00

Now we can convert a relative luminance to an absolute luminance at different energies; therefore, the relative luminances will be reflected easily in the construction of DB.

3. Degradation Experiment at a High Current Density of 100 nA/cm^2

We intended to estimate an expected life by applying severe conditions. We irradiated the samples with intense cathode rays to accelerate the degradation of the phosphor by beta rays. To do this, three different thicknesses were chosen. Two of them were 20 and 45 μm, which are the thicknesses of commercial products, and the other was 10 μm, which showed the strongest luminosity. After the samples were prepared, they were irradiated with a high flux of cathode rays. The detailed conditions are shown in Table 6.

Fig. 6 shows the luminance degradation of the phosphor film by a continuous irradiation of an intense cathode ray. The irradiated current density was 100 nA/cm^2, which is about 250 to 340 times greater than that of the commercial products (See Table 1). The luminance of the 10 μm film was initially much higher than that of the 20 and 45 μm films. On the other hand, the decreasing rate of the luminance on the 10 μm film was more drastic than of the 20 and 45 μm films. From Fig. 6 we estimated the times when the luminance was decreased to half of the initial value. They are 81.3 h, 85.4 h, and 116.8 h for the 10, 20, and 45 μm films, respectively. If we assume that the degradation of phosphor is proportional to the energy transferred to the phosphor by a cathode ray, we can translate the increase of the current density into the acceleration of the time. In other words, the degradation of the phosphor was accelerated by about 250 to 340 times compared to the commercial products. Thus, the real time of the luminance to be reduced to a half of the initial value will be 29,408 h (3.36 year), and 21,786 h (2.49 year) for the 20, and 45 μm films, respectively. (There are no 10 μm commercial products.) Even though we used a constant current density in the experiments, the current density in the commercial products decreases as the tritium decays. Thus, we should also consider the decrease of current density in estimating the life of SLGT. This decrease of the current density will lengthen the life of SLGT; however, the effect of a current density decrease is so small that the difference is negligible.

Table 6. Experimental conditions

Items \ Coating thickness	10 μm, 20 μm, 45 μm
Drying conditions	Temp: 130 °C, Time: 30 min (in convection oven)
Calcination conditions	Temp: 580 °C, Time: 30 min (200 mL/min with air purge)
Energy and current density	4 keV, 100 nA/cm^2

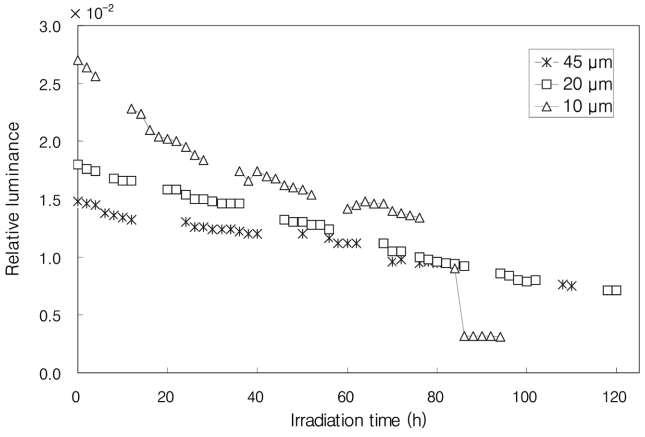

Fig. 6. Luminance at various times by severe conditions (at 4 keV, 100 nA/cm^2).

A drastic degradation of the luminance was observed between 84 h and 86 h for the 10 μm film. After scrutinizing the 10 μm sample we found burnt-out spots on the sample while the other samples did not show such burnt-out spots. We believe that the drastic luminance degradation of the 10 μm sample was caused by these burnt-out spots. These burnt-out spots might be the result of too high energy flux, which heated up the phosphor to its burning point. This would not happen in real systems (commercial SLGTs) so experimental data points in this range can be ignored.

CONCLUSION

First, the relative luminance of the each phosphor film (thickness: 10, 20, 45, 60, 100 μm based on commercial products) was measured at given energies (2, 4, 6, 8 keV) with varying electron fluxes (0.5, 1, 2, 3, 4 nA/cm^2). Regardless of the energies, as the current density increased, and the thickness decreased, the relative luminance increased. The luminance increased as the irradiated en-

ergy increased to 6 keV, and then decreased suddenly at 8 keV. Although this phenomenon has not yet been properly investigated, we assume that the sputtering of the sulfur atoms by incident electrons might be one of the possible explanations based on previous research. We will try to establish this phenomenon through additional experiments.

Second, the absolute luminance was measured at only 4 keV. And a conversion factor of 2,332 was calculated by correlating the absolute and relative luminance at that energy. With this conversion factor the absolute luminance at other energies was estimated. With this conversion, we could use a less expensive relative luminance measuring system to estimate the absolute luminance.

Third, we tried to estimate the expected life of SLGT, which is limited by the reduction of the phosphor efficiency and the amounts of tritium, by additional degradation experiments under severe conditions. The irradiated current density was 2 orders of a magnitude higher than those of the commercial products. The luminance of the 10 μm film was initially much higher than that of 20 and 45 μm. On the other hand, the decreasing rate of the luminance of the 10 μm was more drastic than of the 20 and 45 μm. Burnt-out spots were observed on the 10 μm sample, whereas the other samples (20 and 45 μm) did not show any burnt-out spots.

Now we are constructing DB based on our results, and expecting the development of new products using the newly constructed DB in the future.

ACKNOWLEDGMENT

The authors would like to thank the researchers of the Thin Film Materials Laboratory, Advanced Materials Division, Korea Research Institute of Chemical Technology (KRICT) for providing the CL device and valuable technical consultation. This work was supported by Electric Power Industry Foundation Fund Project of MOCIE.

REFERENCES

Abrams, B. L., Roos, W., Holloway, P. H. and Swart, H. C., "Electron Beam-induced Degradation of Zinc Sulfide-based Phosphors," *Surface Science*, **451**, 174 (2000).

Bingle, R. L., Koops, R. L. and Lynam, N. R., *Safety Release for a Trunk of a Vehicle*, US Patent, 6,390,529 B (2002).

Caffarella, T. E., Radda, G. J. and Dooly, H. H. Jr., *Miniature Radioactive Light Source and Method of its Manufacture*, US Patent, 4,213,052 (1980).

Chung, H., Ahn, D. H., Paek, S. W., Koo, J. H., Kuk, I. H., Lee, H. S. and Kim, K. R., *Use of Tritium in the Production of Self-luminous Compounds*, KAERI /AR-411 (1994).

Hillie, K. T. and Swart, H. C., "Electron Beam Induced Degradation of a Pulsed Laser Deposited ZnS : Cu, Al, Au, Al Thin Film on a Si(100) Substrate," *Appl. Surface Science*, **183**, 304 (2001).

Igarashi, T., Kusunoki, T., Ohno, K., Isobe, T. and Senna, M., "Degradation Proof Modification of ZnS-based Phosphors with ZnO Nanoparticles," *Mater. Research Bulletin*, **36**, 1317 (2001).

Kim, K., Kim, K. S., Son, S. H. and Kim, W.-S., "Manufacturing Process of SLGT Utilizing Tritium Gas: Design of Tritium Handling Facilities," *Korean J. Chem. Eng.*, **21**, 562 (2004).

Kim, K., Lee, S.-K., Chung, E.-S., Kim, K. S., Kim, W.-S. and Nam, G-J., "Tritium Application: Self-Luminous Glass Tube (SLGT)," *Key Eng. Mater.*, **277-279**, 698 (2005).

Kim, W.-S., Jung, Y.-G, Kim, K., Lee, S.-K. and Song, K.-M., KEPRI Report, TM.00NP34.T2001.175 (2001).

Kim, W.-S., Son, S.-H., Kim, K., Lee, S.-K. and Song, K.-M., *Development of Tritium Removal Technology (I)*, 96NJ18 KHNP Report (2002).

McNair, R. C., *Self-luminous Light Source*, US Patent, 4,990,804 (1991).

Oosthuizen, L., Swart, H. C., Viljoen, P. E., Holloway, P. H. and Berning, G. L. P., "ZnS : Cu, Al, Au Phosphor Degradation under Electron Excitation," *Appl. Surface Science*, **120**, 9 (1997).

Son, S. H., Kim, K., Kim, K. S., Shon, C.-H., Yeom, C.-S. and Nam, G-J., *A Domestic Production of SLGT for Rifle View Sights*, Proceedings of 2004 Annual Conference, The Korea Institute of Military Science and Technology, 520 (2004).

South African Standard, *Symbolic Safety Signs, Part 2: Self-luminous (radio -luminescent) Signs*, SABS 1186 (1997).