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Manufacturing Process of Self-Luminous Glass Tube Utilizing Tritium Gas: Optimization of Phosphor Coating Conditions

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Abstract–Domestic research utilizing tritium will become more attractive when tritium is produced from the Wolsong Tritium Removal Facility (WTRF) in Korea, which will start to operate in late 2005. As starting domestic tritium technology research, this study is focused on the mass production of commercially available self-luminous glass tubes (SLGTs) and the design of a new product by simulation. With a low power microscope, SEM-EDX, ICP (Inductively Coupled Plasma) spectrometer, some commercially available SLGTs have been investigated. The inner side of the glass tubes was coated with greenish ZnS phosphor particles with sizes varying from 4-5 μm, and Cu and Al as an activator and a co-dopant, respectively. Besides, the coating thickness is different for each product. and the thickness range of the products to be considered is 10-100 μm. With the phosphor, a binder package was also selected to meet optimal coating conditions. Cathodoluminescence (CL) device (energy: 0-10 keV, electron flux: ~nA) was used to simulate β-ray emitted from tritium. From the CL measurement the optimal conditions were 580-600 °C and 30 minutes. At these conditions the degradation of the phosphor by a heat is minimized. We determined all the coating conditions including the phosphor, binder package, coating thickness, and calcinating temperature for the production of SLGTs. Now we are testing our pilot-scale coating device for a mass production with selected experimental conditions.

Key words: Self-Luminous Glass Tube (SLGT), Tritium, β-Ray, Cathodoluminescence (CL) Device

INTRODUCTION

From the Wolsong Tritium Removal Facility (WTRF) whose construction work began in February, 2003, 5-7 MCi (1 Curi=3.7×10^{10} Bq) of tritium (^{3}H, T) will be produced annually from late 2005. Thus, domestic research related to tritium can be performed more actively [Kim et al., 2002]. Overseas research activity in this area is active, and some products utilizing tritium are being manufactured in the USA, England, Switzerland, and the Republic of South Africa [Bingle et al., 2002; Caffarella et al., 1980; McNair et al., 1991; South, 1997]. Currently, all tritium and tritium containing compounds are imported, and a very small amount (several mCi to less than 1 Ci) is used in the fields of biology, biochemistry, agriculture, calibrating radiological instruments, and synthesizing pharmaceutical products. Tritium containing parts or components with several Ci to several tens of Ci of tritium are also imported and assembled into products such as phosphorescent parts in optical instruments, emergency lights, view sight of army rifles, etc. Therefore, domestic tritium utilization technologies are scarce [Chung et al., 1994; Kim et al., 2001].

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; as a result, they have different atomic masses and physical properties. Natural hydrogen is comprised of 99.958% of protium and 0.015% of deuterium. Tritium, which is a radioactive isotope, is produced both naturally and artificially, but it has a small concentration in the natural environment. Tritium emits beta rays, which are streams of electrons, with 0-18.6 keV (E_{max}: 18.6 keV, E_{mean}: 5.69 keV, E_{mode}: 3.75 keV) energies and 12.323 years of a half time, 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 energy level of tritium is relatively low and the biological effects of tritium on the human body are not significant, which makes tritium a popular radioactive isotope that is used widely in the relevant industries [Lasser, 1989; Sinclair, 1979; Weaver and Wall, 1999]. The electrons in beta ray collide with phosphor to produce light so that the tritium sealed in a phosphor-coated glass tubes can allow the tube to glow without an external supply of energy. The properties of self-luminous glass tubes (SLGTs) can be described as in an advertisement line: "No Wiring, No Electricity, No Batteries, No Switches, No Sunlight, No Maintenance and No Lamps to Replace".

The operating principle of SLGTs is demonstrated in Fig. 1. The light emission mechanism can be explained in three steps: excitation of an activator by an external energy source (beta ray), relaxation of the excited activator, and an emission of light with the energy level which returns to the ground level [Fig. 1(a), (b)]. Tritium can be used in SLGTs as an elemental gas or a metal tritide film

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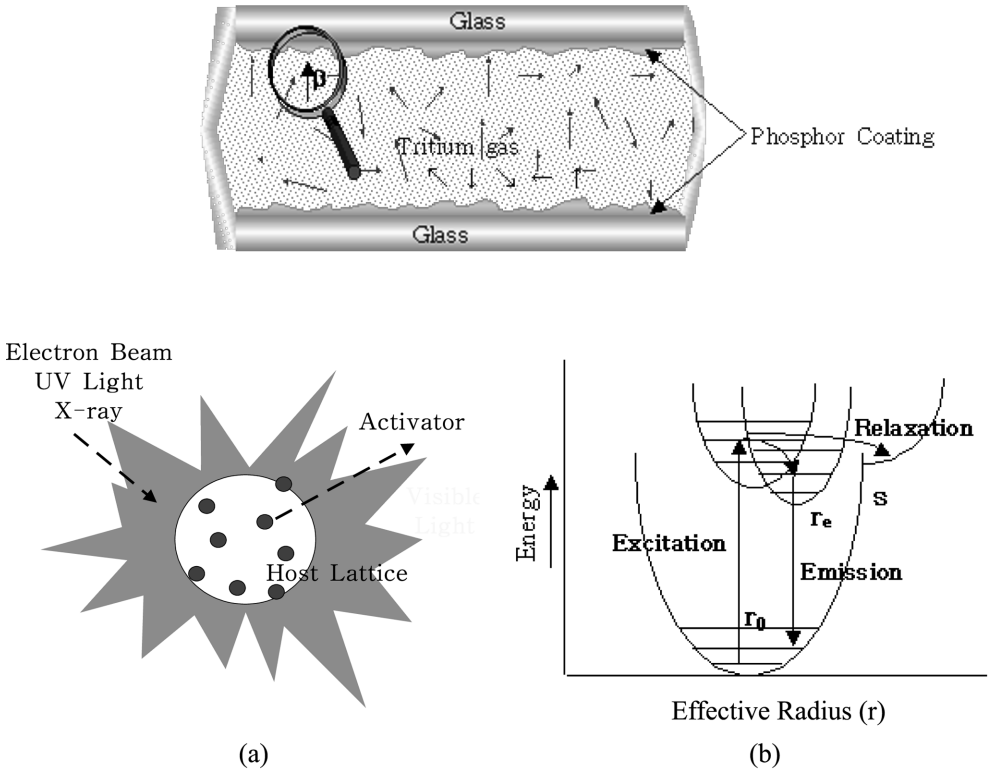


Fig. 1. Structure and operating principle of SLGT.
(a) Structure of phosphor, (b) Light emission mechanism

such as LiT, MgT_2 or TiT_2 [Kherani and Shimayda, 1994; Kherani et al., 1997]. Commercial SLGTs used in emergency exit signs and rifle view sights use elemental tritium gas. However, to manufacture SLGTs a tritium handling system equipped with glove boxes and a tritium clean up system are required to avoid the release of radioactive tritium as well as to adopt a laser sealing/cutting system for mass production of SLGTs.

The characterization and optimization of the phosphor are essential for the development of SLGT manufacturing technology, and the optimum thickness and packing density are required for an effective energy conversion of β-ray. In addition, the binder should have a minimal β-ray absorption, and be able to be used at a low temperature to reduce the phosphor deterioration. Therefore, as the first step of SLGT manufacturing process, characterization and optimization were attempted by using the CL device, and our results will be discussed.

EXPERIMENTAL

1. Composition Analyses and Measurement of the Phosphor Thickness

The inner side of the tube was coated with gold and analyzed with a scanning electron microscope (SEM, JSM 6400, Jeol Co.) equipped with an energy dispersive X-ray spectrometer (EDX). Phosphor powder scraped from the tube was also examined with the SEM. For Inductively Coupled Plasma (ICP) analysis, standard solutions were prepared by diluting Perkin-Elmer 1,000 ppm standard solution. ICP samples were prepared by dissolving the phosphor coated on the inner side of SLGT with a 1 : 1 hydrochloric acid solution to make the total sample volume of 50 mL, and then the samples were analyzed with ICP (ICP-OES: Optima 4300 DV, Perkin-Elmer Instruments) [Kim et al., 2005; Son et al., 2004].

2. Design of Cathodoluminence (CL) Device Including a Sample Holder

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 a 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 electron fluxes in our products are very low as shown in Table 1. As a commercialized CL device cannot meet the experimental conditions, we modified the CL device.

The CL device was equipped with an Auger gun as an energy source, a measuring system to display the CL spectra, a vacuum system, and a feedthrough to measure the current applied to the sam-

Table 1. The current density for the two target 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

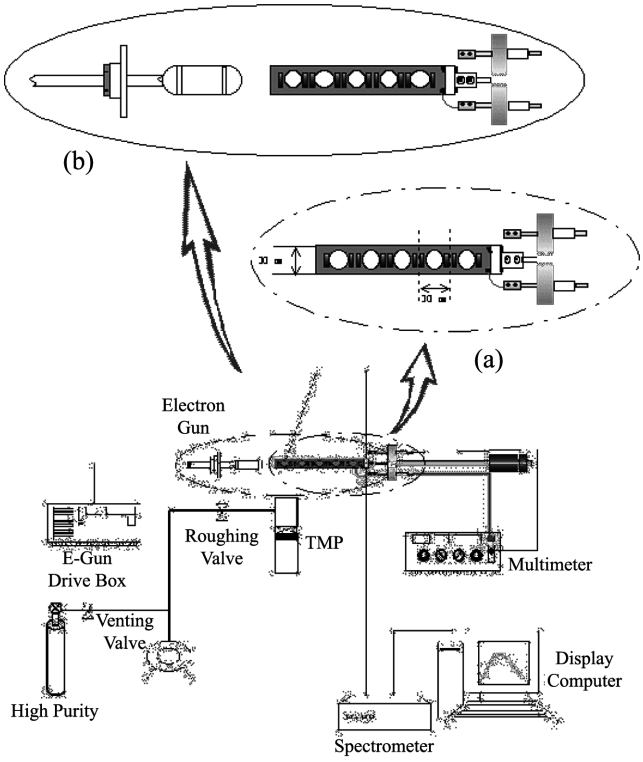


Fig. 2. Device for cathodoluminescence (CL) measurement.
(a) Sample holder, (b) Equip for measuring of spot size

ples. 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(a). 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. The holder was made to move horizontally by a magnet in the chamber. After the samples were mounted, the Roughing valve was opened and the rotary pump was turned-on, and the chamber was evacuated to 10^{-2}-10^{-3} torr. After the vacuum level was stabilized, the turbo molecular pump was turned-on, and the vacuum level was lowered to 10^{-7} torr, and then a voltage was applied to the electron gun. [Abrams et al., 2000; Hillie and Swart, 2001; Igarashi et al., 2001; Oosthuizen et al., 1997].

3. Determination of the Spot Size

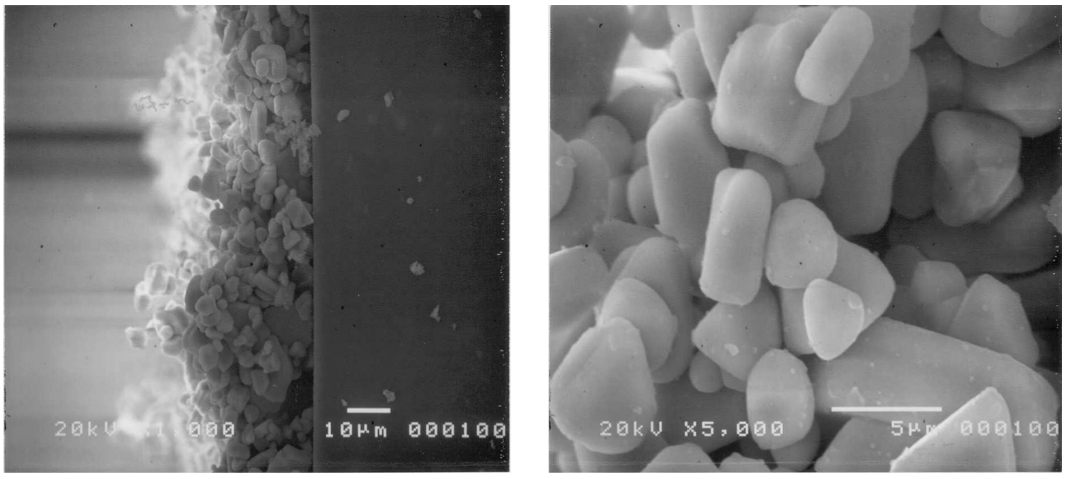
The necessary information for these studies is the current and the current density applied to a phosphor film. Since the current density is the current per unit area, the spot size of the cathode ray needs to be measured. The spot size was determined by measuring the current variation of a metal target. The metal target was made by inserting a thin metal film between the ceramic plates as shown in Fig. 2(b). A spot size could be determined by scanning the spot with the metal target with a 0.1 mm interval and measuring the current with a multimeter.

RESULT AND DISCUSSION

1. Composition Analyses and Measurement of the Phosphor Thickness

As shown in Fig. 3(a), the coating surface of SLGTs was not uniform. Measurement using a stereozoom microscope showed that the maximum thickness of the coating is about 20 μm (Type A) and 45 μm (Type B), respectively. The phosphor particle sizes in Fig. 3(b) were also not uniform and the average size was about 4-5 μm.

SEM-EDX (Fig. 4) showed that the major elements in the phosphor were Zn, S, Al, Cu, and Si. The result of the quantitative analyses of the phosphor by ICP is presented in Table 1. The major component is Zn, implying that ZnS is the phosphor. Two minor components Al and Cu, whose relative mole% for the Zn are 0.04 and 0.03, respectively. The mole percents of Al and Cu for the Zn were closely matched with commercially available Kasei's ZnS: Cu, Al. Si observed in SEM-EDX seemed to come from the glass debris produced during the cutting of the tube and the lower concentration (Ca: 0.01, Ba: 0.004, P: 0.07 mg/L) than the detection limits indicated as N/A in Table 2. Here, the oxygen peak on SEM-EDX was presumed to have come from a native oxygen layer due to an



(a) (b)

Fig. 3. (a) SEM feature of the surface of SLGT (×1,000), (b) SEM feature of the surface of SLGT (×5,000).

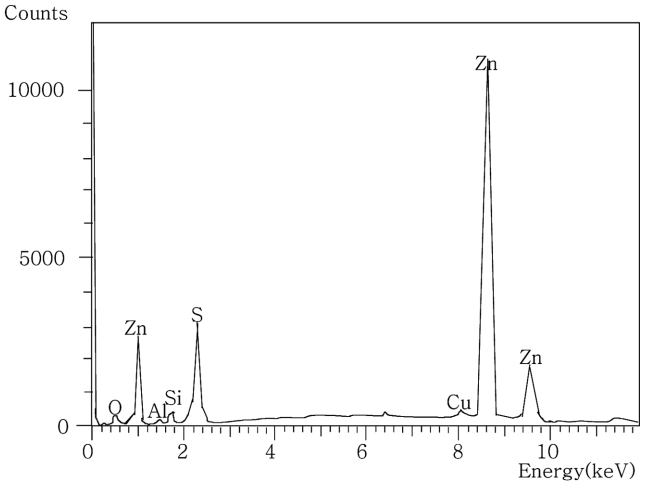


Fig. 4. SEM-EDX analysis of SLGT coating.

Table 2. Composition of SLGT coating by ICP

Items \ Element	Concentration (ppm)	Concentration (mmole)	mole% (based Zn)
Zn	493.29	0.3773	100.00
Cu	0.15	0.0001	0.03
Al	0.09	0.0002	0.04
Ca	0.00	N/A	N/A
P	1.28	0.0019	0.50
Ba	0.00	N/A	N/A

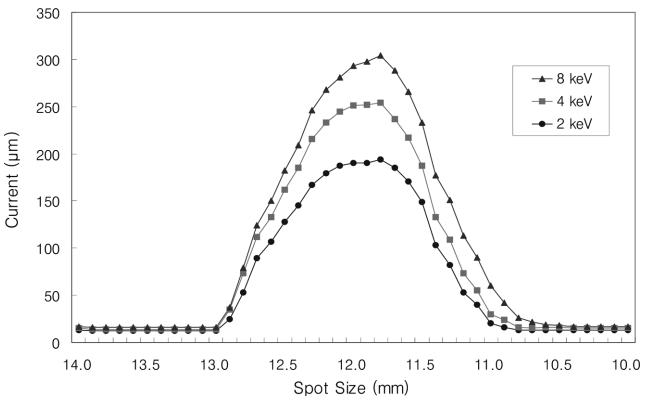


Fig. 5. Spot size at different energies (2, 4, and 6 keV).

air exposure.

2. Determination of Spot Size

The spot sizes for 2 keV, 4 keV and 8 keV are shown in Fig. 5. The sizes were measured three times at each energy, and averaged. As shown here, the sizes were almost the same regardless of the applied energies, and the diameter of the spots was 2 mm. Therefore, the spot size used to calculate the current density in these studies was a radius of 1 mm, and an area of 3.14 mm^2.

3. Determination of the Calcination Conditions

The suitable calcination temperature and time to prevent a deterioration of the phosphor by a heat and to remove the residual substances such as carbon were determined by CL experiments. The

Table 3. Experimental conditions for the calcination temperature

Coating thickness	20 μm
Drying conditions	130 °C/30 min (in convection oven)
Calcination conditions	Temp: 580, 600, 630, 650, 680 °C (30 min, 200 mL/min with air purge)
Energy and electron density	4 keV, 3 nA/cm^2

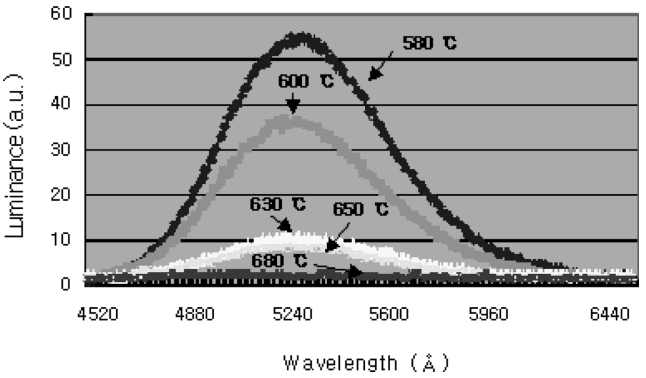


Fig. 6. Cathodoluminescence spectra at different temperatures (Coating thickness: 20 μm).

coating thickness was fixed at 20 μm, based on a commercial product. The CL was measured at different temperatures with 20-30 °C intervals. The range of calcinating temperature was chosen between 580 and 680 °C, based on the physical properties of the used binder package and glass tubes. As the firmness of a coating could not get below 580 °C, the CL experimental was started at 580 °C. The air was injected at a rate of 200 mL per 1 minute, and the sample was calcinated for 30 minutes at each temperature considering the coating firmness. The vacuum was kept at 2.3×10^{-7} torr, the energy and electron density were 4 keV and 3 nA/cm^2. The other detailed conditions are shown in Table 3.

The CL results from different temperatures at a fixed thickness of 20 μm are shown in Fig. 6. The maximum peak was 5,300 Å, which indicates a green phosphor spectra. The maximum peak did not depend on the temperature change, but the deterioration at different temperatures was remarkable. Particularly, a sharp reduction in the luminance was observed at 630 °C, and a peak at 680 °C was not observed. The calcination temperature was decided upon as 580-600 °C.

4. Evaluation of the Thickness and the Calcination Time Effects

To observe the effects of a coating thickness on the luminance at 580-600 °C, the CL was measured at a different thickness varying from 10 (min)-100 μm (max). The vacuum was 3.4×10^{-7} torr, the energy and current density were 4 keV and 3 nA/cm^2, respectively. The other detailed conditions are shown in Table 4.

The results from several calcinating time periods at a fixed thickness and temperature are shown in Figs. 7 and 8. The vacuum was 3.4×10^{-7} torr and 2.8×10^{-7} torr, and the energy and electron density were 4 keV and 3 nA/cm^2 respectively. As shown in Fig. 7, the main peaks were not moved and the CL looked almost the same at 10, 20 and 30 minutes. However, the luminance at 60 and 180 minutes was markedly reduced On the other hand, the luminances of 100

Table 4. Experimental conditions for the coating thickness

Coating thickness	10 μm, 100 μm
Drying conditions	130 °C/30 min (in convection oven)
Calcination conditions	580 °C, 200 mL/min air purge Time : 10, 20, 30, 60, 180 min
Energy and electron density	4 keV, 3 nA/cm^2

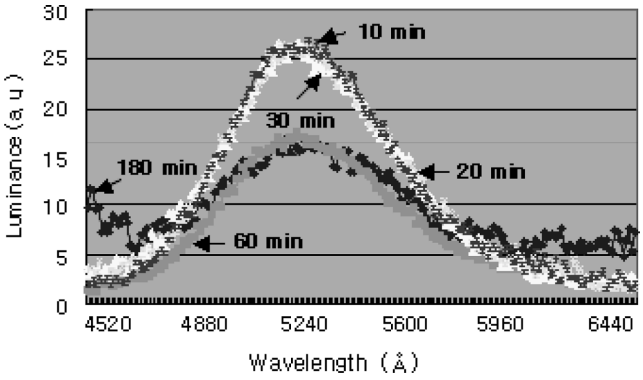


Fig. 7. CL spectra at different times (10 μm).

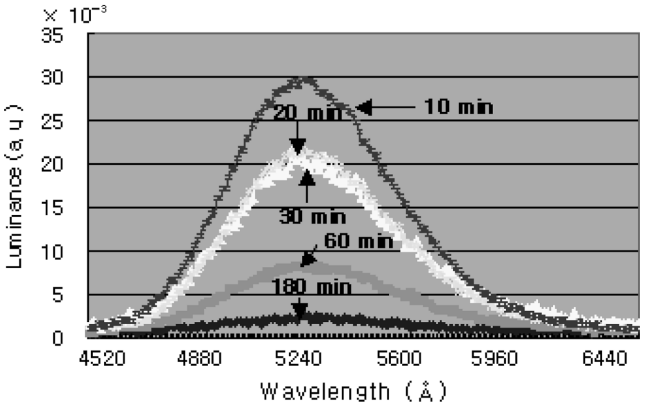


Fig. 8. CL spectra at different times (100 μm).

μm thickness at the same conditions were decreased depending on the thickness as shown in Fig. 8. Particularly, when the time was 60 minutes, the luminance was decreased to 70%.

CONCLUSION

We found that the commonly used phosphor for SLGTs is ZnS: Cu, Al, and the mean particle size was 4-5 μm through ICP and SEM analyses. And also, the coating thickness varied widely among the commercial products, and the thicknesses of our target products were 10-100 μm. In addition, we selected a suitable binder to the phosphor, and screen-printed samples on ITO glass plates were prepared to establish the optimal coating conditions. To do this, we used CL devices (energy: 0-10 keV, electron flux: ~nA) based on considering that the β-ray emitted from tritium corresponds to an electron flow. The optimal conditions were determined as 580-600 °C and 30 minutes to remove the binder without degrading the phosphor by a heat. All the coating conditions such as the phosphor, binder package, coating thickness, and calcinating temperature for the production of SLGTs have been determined. Now we are testing our pilot-scale coating to establish the optimum conditions for mass production.

In other areas of our SLGT research, the conceptual design of a tritium handling system is about to be completed and the procedures and documents for a Korea Institute of Nuclear Safety (KINS) license for the use of tritium are being prepared, and also the cutting and sealing technology using a laser is in progress [Kim et al., 2004].

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