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Review

The recycling of rare earths from waste tricolor phosphors in fluorescent lamps: A review of processes and technologies

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ABSTRACT

Rare earths have become the most important strategic resources, widely used as functional materials in industry and many other aspects of life due to its optical, electrical, and magnetic characteristics. As a consequence, a considerable number of wastes containing rare earths such as abandoned fluorescent lamps are generated and lost. Considering the scarcity in availability and supply of certain raw materials, waste tricolor phosphors are viewed as potential resources that can be mined in urban areas for their reutilization as rare earths. A number of studies in this area have been carried out all over the world.

The purpose of this paper is to review the current status of recycling technologies of rare earths from waste tricolor phosphors in fluorescent lamps. The main characteristics of the tricolor phosphors were introduced, and also a detail review of the typical single recycling and reusing technologies with regard to waste tricolor phosphors was carried out in present paper. After that, several combined recycling processes and technologies were evaluated. Based on the review, the prospects of recycling technologies were suggested.

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1. Introduction

Rare earths have become the most important strategic resources (Alonso et al., 2012). Based on their optical, electrical and magnetic characteristics (Saini et al., 2006; Croat et al., 1984), rare earths have been widely used as functional materials in many fields such as electronic information, metallurgical machinery, petrochemical industry, energy and environment, national defense and so on (USGS, 2002; Chen, 2011). China as a country used to be abundant in rare earth minerals in the world. However, the reserve is rapidly decreased due to factors such as increase in consumer demand (Yan et al., 2006), a large number of cheap exports (Hong, 2006), long-term predatory exploitation (Tse, 2011; Du and Graedel, 2011). The reserve of rare earth minerals in China was accounted for 74% of the total world amount in 1970s and this has dropped to 23% during the past 50 years (Yan et al., 2011; Xie, 2011; Information Office of the State Council of the people's Republic of China, 2012). According to the calculation by Association of China Rare Earth Industry (ACREI), China supplied almost 95% rare earth resources for the global market in 2009. On the other hand, the scraps of some typical rare earth products, such as luminescent materials and permanent magnetic materials, are increasing (Itoh et al., 2008; Binnemans et al., 2013; Brunner, 2011). For instance, 7% of the global rare earth minerals was known to be the phosphors from 2006 to 2008, while its cost accounted for 32% of the rare earth product cost (Schüler et al., 2011; The Chinese Society of Rare Earths, 2006, 2007, 2008). According to statistics, the average service life of a fluorescent lamp is 3000–5000 h (about three years) in China (Mao, 1998), and there are approximately 4 g tricolor phosphors per fluorescent lamp (Raposo et al., 2003). In 2011, about 4800 million fluorescent lamps were scraped (Wang and Zheng, 2010; Zhang, 2012). With reference to the domestic market price of rare earths by the end of the year (China Rare earth metal prices, 2011), the value of rare earths contained in the waste fluorescent lamps was more than 1600 million dollars. If these can be recycled and re-used efficiently, it will not only reduce the exploitation of primary rare earth minerals, but also build the circular-utilization industrial chain of abandoned rare earths, which will greatly help improve the efficient utilization of rare earth resources.

A number of studies on recycling of rare earths have been carried out all over the world. Japan enacted the "Waste Disposal Law" and "Improve Resource Utilization Efficiency Law" for the recovery of rare earth materials in the national scope and the development of recycling technologies about secondary rare earth resources (Bai, 2004; Yamasue et al., 2009). Britain, Canada and many other countries established websites related to the waste fluorescent lamp recycling, which described and guided the behaviors of fluorescent lamp producers, users, and the recycling outlets (RCO, 2013; Recolight, 2013). With the rapid development of the circular economy in China (Zuo and Feng, 2008; Jin and Jakob, 2006), the secondary utilization of rare earth fluorescent powders is being put on the agenda gradually (GB/T 22908, 2008). The ideas have been put forward in the eighteenth National Congress of the Communist Party of China. These include taking the ecological civilization construction into consideration, promoting resource conservation and developing the circular economy, promoting reduction, reuse and recycle in processes of production, circulation and consumption (Hu, 2012). "The special planning in science and technology project of waste resource utilization in Twelfth Five-year plan", published by the Ministry of Science and Technology of the People's Republic of China, 2012, pointed out clearly that the development of recycling technologies of waste rare earth luminescent materials will be focused on, especially on the development of the separation technology of selective leaching of lanthanum, praseodymium and cerium. ACREI pointed in 2013 that development will focus on production processes of tricolor fluorescent powders which are of low cost and highly utilize rare earth materials. That means the closed cycle of "tricolor fluorescent powders – Waste – secondary rare earth resource "will result in the effective utilization of rare earth resources and reduce pollution massively.

This paper introduces the basic composition of the aluminate system tricolor phosphors, summarizes the current status of recycling and reusing technologies of waste tricolor phosphors and the rare earths inside; analyses and evaluates several recycling processes and technologies. Meanwhile, the prospects of future studies on recycling technologies have been put forward, aiming at providing suggestions for further technological development for effective utilization of secondary rare earth resources and products.

2. Tricolor phosphors – mechanism and composition

Tricolor phosphors are generally coated as a thin layer inside a fluorescent lamp, as presented in Fig. 1 (Tunsu et al., 2012). The phosphors in the lamp absorb the invisible UV energy emitted from the interaction of mercury (Hg) and electrons, and convert it into visible light.

Generally, tricolor phosphors can be divided into four categories. These are the phosphate, aluminate, borate and silicate systems (Justel et al., 1998; Yu and Chen, 1995; Ronda, 1995). Differences in molecular formula of the four tricolor phosphors are presented in Table 1 (Tian, 2012). Borate and silicate system have been not developed completely. Phosphate and aluminate system are used alone or mixed most commonly. However, Phosphate system has both poor color rendering property and poor stability under high voltage. The aluminate system has gradually become the most widely circulated in the world because of its advantages of anti-ultraviolet aging, high stability under high temperature, high intensity of ultraviolet irradiation and high luminous efficiency (Zhao, 2010). Therefore, the key and difficult points of recovery will concentrate on aluminate system.

The light-emitting mechanism of aluminate system has already been reviewed (Ronda et al., 1998). The red emission in these lamps is generated by $Y_2O_3{:}Eu^{3+}$. Here, excitation involves a charge transfer transition from O^{2-} ions to Eu^{3+}. Emission takes place within the f-levels of the Eu^{3+} ions. $BaMgAl_{10}O_{17}$ doped with Eu^{2+} (BAM) is used as blue emitting phosphor, in which the photons are absorbed

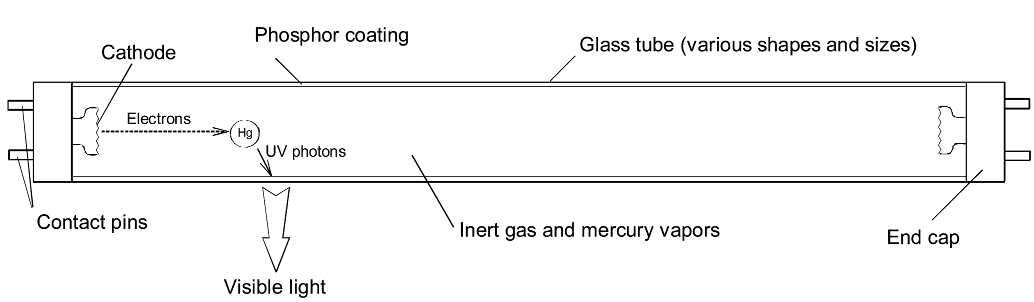

Fig. 1. Diagrammatic representation and operation principle of a fluorescent lamp (Tunsu et al., 2012).