Emission behaviour of brominated compounds in thermal treatment of printed circuit board under inert and oxidative atmosphere

O. Terakado*, H. Takagi and M. Hirasawa

Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Japan
e-mail: teramon@numse.nagoya-u.ac.jp; phone & fax: +81-52-789-3250

Abstract

In the view of the emission control in thermal treatment of wastes electrical and electronic equipment, thermal degradation of a printed circuit board has been studied both in inert and oxidative atmosphere. The presence of oxygen in atmosphere reduces the yield of hydrogen bromide, a major brominated comopound in pyrolysis treatment, and enhances the formation of bromine as well as hypobromous acid. The presence of zinc oxide in sample results in the formation of zinc bromide. Moreover, the release of brominated compounds is promoted in comparison to the case of pure PCB.

Keywords: *Printed circuit board, Brominated flame retardant, Hydrogen bromide, Bromine, Emission control*

1. Introduction

Waste electrical and electronic equipment, WEEE, contains variety of valuable metals, so that the development of the metal recovery process is of great importance for the establishment of sustainable society. Various processes have been proposed so far: conventional ones are based on the hydrometallurgical treatment after the combustion of WEEE. It should be noted that many flame retardants are used in electrical and electronic equipments in order to ensure their fire safety. In general, the share of brominated flame retardant, BFR, reaches up to 40 % [1], so that special attention should be paid in the thermal treatment of WEEE.

In the course of our studies on the application of metal oxides to the halogen fixation in pyrolysis of halogen-containing polymer, we have found that bromine originating from tetrabromobisphenol A, a typical BFR, and a printed circuit board containing BFRs can be fixed in the form of stable metal halide or oxyhalide [2,3].

In the present work, we have carried out thermal treatment of a printed circuit board, PCB, under inert and oxidative atmosphere in the presence of metal oxide. The influence of atmosphere and oxides are compared and discussed.

2. Materials and Methods

Printed circuit boards, containing BRRs, were kindly supplied from Hitachi Kasei Co., Ltd. They are FR-4 type samples, where epoxy resin is reinforced by woven glass fibres. The copper plate was coated on the board, which was removed by iron chloride aqueous solution in the present study. The copper-free PCB was crushed and ground down to less than 250 μm. The powder was mixed with metal oxide powder (Kanto Chem. Co., Ltd. or Kishida Chem. Co., Ltd.). As an example, the composition of zinc oxide was 2.6 mass%, which corresponds to the stoichiometric ratio for the formation of $ZnBr_2$.

Themogravimetric analysis, TGA, has been carried out with TGA-2050 equipment (TA Instruments) at the heating rate of 10 °C/min under the atmosphere of helium-oxygen mixture. Thermal decomposition experiments were carried out with a horizontal type reactor (700 mm in length and 26 mm in i.d.) under helium and air atmosphere. The experimental set-up is as same as that described elsewhere [2]. The hydrogen bromide captured in a water trap was monitored through the amount of bromide ion, Br^-, with an ion meter (IM-40S, TOA Electronics). The hypobromous acid, HBrO, in the trap was determined by iodometry [4]. The bromine adhered at the cold part of the reactor was collected with pure water, and converted to bromide ion by the irradiation of light into the solution, whose ion concentration was then determined by the ion meter. The char after thermal treatment was characterized by XRD (XRD-6100, Shimadzu) and FT-IR (FT-IR 230, JASCO) analysis.

3. Results and Discussion

Fig. 1 shows the result of TGA of PCB specimen at different oxygen partial pressure. The mass reduction around 310-350 °C is due to the thermal decomposition of epoxy resin. Obviously, this decomposition stage is independent of atmosphere, because the mass reduction behaviour is essentially the same. However, the mass after this stage is higher in the presence of oxygen, which suggests the formation of oxygen-containing functional groups in the char, as observed also in the oxidative treatment of ABS resin [4]. This is confirmed by an FT-IR analysis of the char obtained from a sample

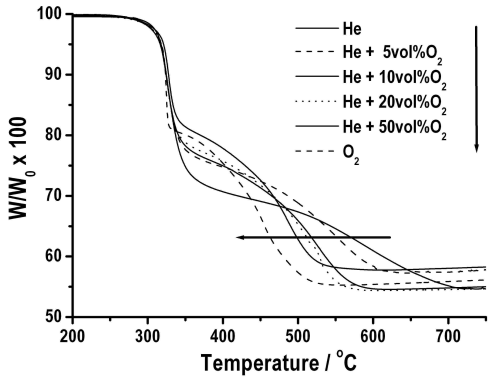

Fig. 1 Results of TGA of PCB at the heating rate of 10 °C/min under different atmosphere. The curve assignment follows the order of the arrow on the graph.

heated at 370 °C under 50%O_2-He atmosphere, where the increase in the peak intensity at 1750 cm^{-1}, assigned to the C=O stretching mode, was observed.

On the other hand, the second mass reduction stage around 400-600 °C is strongly influenced by the atmosphere in the gas phase. The mass reduction rate becomes higher with increasing oxygen partial pressure. The result indicates that this mass reduction stage involves the oxidation of char matrix formed at the first mass reduction stage.

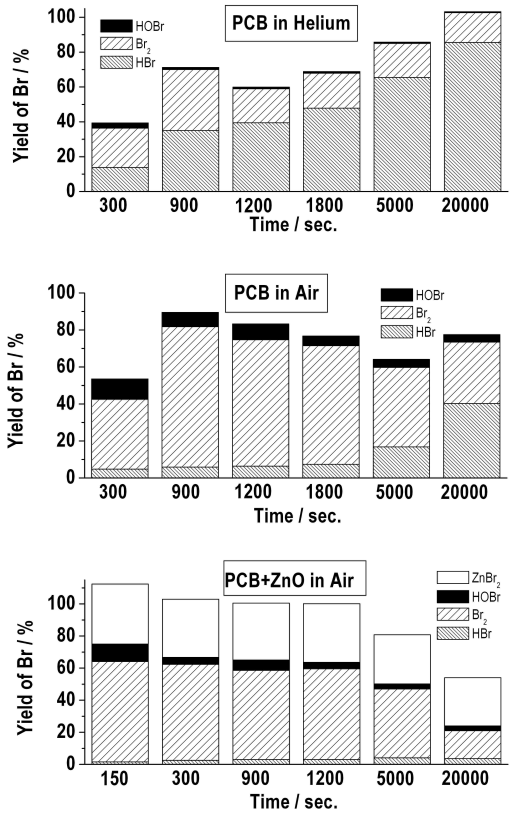

Fig. 2 Yield of major brominated compounds at different reaction time.

As known in literature [3,5], pyrolysis treatment of PCB results in the formation of hydrogen bromide with by-products of brominated organic compounds.

The presence of oxygen in the atmosphere gives rise to the significant change in the distribution of brominated compounds, and the yield of bromine increases with increasing oxygen concentration in the gas phase [6].

Fig. 2 shows the yield of hydrogen bromide, bromine and hypobromous acid evolved at different reaction time of thermal treatment of pure PCB under inert and air atmosphere and PCB-ZnO mixture under air atmosphere, respectively.

The gradual increase of HBr with increasing treatment time of pure PCB under helium is in consistent with our previous observation [3]. It is noteworthy that bromine is also formed in thermal treatment under inert atmosphere.

On the other hand, the yield of HBr is considerably low in thermal treatment of pure PCB under air atmosphere. Obviously, the oxidation of Br^- takes place in this case, since the yield of Br_2 and HOBr is higher. Furthermore, the amount of bromine in the reactor decreases apparently with increasing reaction time. This is probably due to the evaporation of volatile bromine.

The presence of zinc oxide leads to the formation of zinc bromide. The release of brominated compounds completes obviously at 150 sec in contrary to the sample without oxide. It is therefore considered that the addition of the oxide enhances the decomposition of PCB. It should be noted that high portion of bromine remains in the reactor. Thus, attention should be paid in thermal treatment waste PCBs.

4. Conclusions

In the present work, we studied the emission behaviour of brominated compounds in thermal treatment of printed circuit board in inert and oxidative atmosphere. It was found that the presence of oxygen leads to the oxidation of hydrogen bromide to bromine or hypobromous acid. The bromine remains in the cold part of the furnace and gradually evaporates. The intentional addition of oxide, such as ZnO, leads to the fixation of bromine, and apparently promotes the release of brominated compounds from PCB.

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